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ADVANCED PHYSCIAL CHEMISTRY

Author
Dr. T. Stalin
Assistant Professor
Alagappa University
Karaikudi

ADVANCED PHYSICAL CHEMISTRY

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1.0 Introduction

In thermodynamics, **statistical thermodynamics** is the study of the microscopic behaviors of thermodynamic systems using probability theory. Statistical thermodynamics, generally, provides a molecular level interpretation of thermodynamic quantities such as work, heat, free energy, and entropy. Statistical thermodynamics was born in 1870 with the work of Austrain physicist Ludwig Boltzmann, much of which was collectively published in Boltzmann's 1896 Lectures on Gas Theory.

1.1 Objectives

After going through this unit, you will be able to:

- Understand about the statistical thermodynamics
- Understand the Microscopic behaviour of thermodynamic system using probability theory.
- Explain the concept of Negative Kelvin Temperature
- Explains the microstates and configuration

1.2 Maxwell – Boltzmann Distribution

Postulates:

1. The system considered is an isolated system of independent, non interacting identical particles without spin in equilibrium at a definite temperature.
2. The particles are distinguishable

NOTE

3. There is no restriction to the number of particles which may occupy any given quantum state. Let us consider any ideal gas containing N identical distinguishable independent particles. let at any instant

n_o particle have energy E_o

n_1 particles have energy E_1

.

.

.

n_i particles have energy E_i

Total number of particles in the system is

$n_o + n_1 + n_2 + n_3 +$ ----------n_i + --- =N

$$\sum_{i=0}^{\infty} n_i = N$$

Total number of particles in the system is assumed to be constant and hence

$$\sum_{i=0}^{\infty} \partial n_i = 0 \quad \rightarrow (1)$$

This is the first condition of constraint.

4. Total energy possessed by all the molecules E is

$$E = E_0 n_0 + E_1 n_1 + \quad + E_i n_i + \quad = \sum_{i=0}^{\infty} E_i n_i$$

5. Total energy is constant and hence $\partial E = 0$

$$\sum_{i=0}^{\infty} E_i \partial n_i = 0 \rightarrow (2)$$

This is the second condition of constraint.

6. he system is considered at statistical equilibrium and hence thermodynamic probability will be maximum.

1.2.1 Maximization of thermodynamic probability

For Non - degenerate energy levels:

The probability of distribution of particles among the quantum states is proportional to the number of different ways in which the molecules can be arranged under the specified conditions. The number of ways in which 'N' distinguishable particles can be arranged in different energy levels such that n_o particles are in the ground state , n, in the 1^{st} , n_2 in the 2^{nd} and so is given by

$$W = \frac{N!}{\pi_{i=0}^{\infty} n_i!} \times cons\tan t$$

$$\ln W = \ln N! - \ln(\pi_{i=0}^{\infty} n_i!) + cons\tan t$$

Applying stirlings approximation formula

$$\ln N! = N \ln N - N$$

$$\ln W = N \ln N - N - \sum_{i=0}^{\infty} \ln(n_i!) + cons\tan t$$

$$= N \ln N - N - \sum_{i=0}^{\infty} (n_i \ln n_i - n_i) + cons\tan t$$

$$= N \ln N - N - \sum_{i=0}^{\infty} n_i \ln n_i + \sum_{i=0}^{\infty} n_i + cons\tan t$$

When the system attains statistical equilibrium there will be most probable distribution and thermodynamic probability will be maximum and hence variation in W

i. ∂ω or ∂lnω is zero.

$\partial \ln \omega = 0$

NOTE

$$\partial \ln \omega = \partial(N \ln N) - \partial(\sum_{i=0}^{\infty} n_i \ln n_i) + constant$$

$$= 0 - \sum_{i=0}^{\infty}(n_i \cdot \frac{1}{n_i} + \ln n_i)\partial n_i = 0$$

$$= -\sum_{i=0}^{\infty} \ln(n_i)\partial n_i = 0 \qquad \sum_{i=0}^{\infty} \partial n_i = 0$$

(or)

$$\sum_{i=0}^{\infty} \ln(n_i)\partial n_i = 0 \rightarrow (3)$$

This is the 3rd condition of constraint. For a system of maximum thermodynamic probability and for a stem in statistical equilibrium condition 1, 2&3 must be satisfied.

When there are more than two conditions, lagrangian method of undetermined multiplers is used to solve the problem.

Equation (1) is multiplied by α, equation (2) is multiplied by β and combined with equation (3) we get

$$\alpha\sum_{i=0}^{\infty}\partial n_i + \beta\sum_{i=0}^{\infty} E_i\partial n_i + \sum_{i=0}^{\infty}\ln(n_i)\partial n_i = 0$$

$$\sum_{i=0}^{\infty}(\alpha + \beta E_i + \ln n_i)\partial n_i = 0$$

Since, the variations ∂n_1, ∂n_2, ∂n_3 etc are independent of each other, provided the conditions (1) & (2) are satisfied, the co- efficient of ∂n_1's must be zero and $\partial n_i \neq 0$

$$\alpha + \beta E_i + \ln n_i = 0$$

$$\ln n_i = -\alpha - \beta E_i$$

$$n_i = e^{-\alpha - \beta E_i} \qquad (\alpha = \frac{-\mu}{RT}, \beta = \frac{1}{KT})$$

$$n_i = ce^{-\beta E_i} = e^{+\mu/RT}.e^{-E_i/KT}$$

The factor $e^{-E_i/KT}$ is called Boltzmann factor and R is the Boltzmann constant, the expression

$n_i = e^{-\alpha}.e^{-\beta E_i} = \exp^{(-\alpha)}.\exp^{(-\beta E_i)}$ is called Maxwell – Boltzmann distribution law for the system having N distinguishable particles distributed in non degenerated energy levels.

The total energy or any individual form of energy is given as

$$E_{(Total)} = E_{elec} + E_{vib} + E_{rot} + E_{trans}$$

1.2.2 When the energy levels are degenerate

The number of ways in which 'N' distinguishable particles can be arranged in different energy levels having the degeneracy g_o, n, in the first state having the degeneracy g_1, n_2 in the 3^{rd} having the degeneracy g_2 and so on i.e. given by

$$W = N! \pi_{i=0}^{\infty} g_i \frac{n_i}{n_i!} \times cons\tan t$$

$$\ln W = \ln(N! \pi_{i=0}^{\infty} g_i \frac{n_i}{n_i!} \times cons\tan t)$$

$$= \ln N! + \ln \pi_{i=0}^{\infty} g_i^{n_i} - \ln \pi_{i=0}^{\infty} n_i! \times cons\tan t$$

$$= \ln N! + \sum_{i=0}^{\infty} n_i \ln g_i - \sum_{i=0}^{\infty} \ln n_i! + cons\tan t$$

Applying Stirlings approximation Formula for evaluation

of factorials of large number we get

NOTE

$$\ln N! = N \ln N - N$$

$$\ln W = N \ln N - N + \sum_{i=0}^{\infty} n_i \ln g_i - \sum_{i=0}^{\infty} (n_i \ln n_i - n_i) + constant$$

$$= N \ln N - N + \sum_{i=0}^{\infty} n_i \ln g_i - \sum_{i=0}^{\infty} n_i \ln n_i + \sum_{i=0}^{\infty} n_i + constant$$

$$= N \ln N + \sum_{i=0}^{\infty} n_i \ln g_i - \sum_{i=0}^{\infty} n_i \ln n_i + constant$$

When the system attains statistical equilibrium there will be most probable distribution and thermodynamic probability will be maximum, i.e. variation in law will be zero.

$$\partial W = 0$$

(or) $\partial \ln W = 0$

$$\partial \ln W = \partial N \ln N + \partial \sum_{i=0}^{\infty} n_i \ln g_i - \partial \sum_{i=0}^{\infty} n_i \ln n_i + \partial (constant) = 0$$

$$= 0 + \sum_{i=0}^{\infty} \ln g_i \partial n_i - \sum_{i=0}^{\infty} (1 + \ln n_i) \partial n_i + 0 = 0$$

$$= \sum_{i=0}^{\infty} \ln g_i \partial n_i - \sum_{i=0}^{\infty} \ln n_i \partial n_i = 0$$

$$= \sum_{i=0}^{\infty} \ln (g_i / n_i) \partial n_i = 0$$

(or)

NOTE

$$-\sum_{i=0}^{\infty}\ln(g_i/n_i)\partial n_i = 0 \rightarrow (3)$$

This is the 3rd condition of constraint

For a system of maximum thermodynamic probability and for a system in statistical equilibrium conditions 1, 2 & 3 must be satisfied

When there are more than two conditions Lagrange's methods of undetermined multipliers is used to solve the problem.

Equation (1) is multiplied by α, equation (2) by β & combined with equation (3)

$$\alpha\sum_{i=0}^{\infty}\partial n_i + \beta\sum_{i=0}^{\infty}E_i\,\partial n_i - \sum_{i=0}\ln(\frac{g_i}{n_i})\partial n_i = 0$$

$$\sum_{i=0}^{\infty}(\alpha + \beta E_i - \ln(g_i/n_i)\partial n_i = 0$$

Since the variations ∂n_1, ∂n_2, ∂n_3 etc are independent of each other, provided the conditions 1 &3 are satisfied the coefficient of ∂ni's must be equal to zero. $\partial ni \neq 0$.

$$\alpha + \beta E_i - \ln(g_i/n_i) = 0$$

$$\ln(g_i/n_i) = \alpha + \beta E_i$$

$$g_i/n_i = e^{\alpha+\beta E_i}$$

$$n_i = \frac{g_i}{e^{\alpha+\beta E_i}} = g_i e^{-\alpha-\beta E_i} \qquad (\alpha = \frac{-\mu}{RT}, \beta = \frac{1}{KT})$$

$$= g_i e^{+\mu/RT}.e^{-E_i/KT}$$

Where, g_i is the degree of degeneracy or statistical weight factor for the ith level. This expression is called Maxwell Boltzmann

distribution law. It gives the number of particles in the ith level with degeneracy g_i having energy E_i and

NOTE

$$E_{i(Total)} = E_{elec} + E_{vib} + E_{rot} + E_{trans}$$

1.3 Negative Kelvin Temperature

According to Maxwell Boltzmann statistics the equilibrium population of two levels is given by

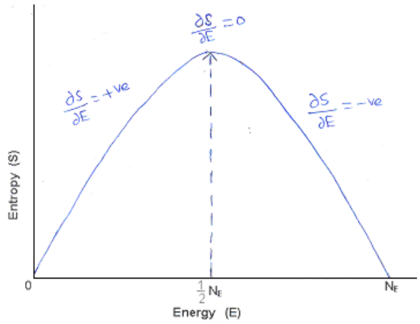
$$\frac{n_i}{n_0} = e^{-E_i/KT}$$

Where n_i is the number of particles in the upper ith level and n_o is the number of particles in the lowest level at temperature T and E_i is the energy of the ith level in excess of zero point level. At T = 0 ni/no=0 that is all the molecules will be in the ground state as $T \rightarrow \infty$ n_i/n_o =1 and the population of the states will be equal.

In general in any system at statistical equilibrium the higher level will be occupied by lesser number of particles than the lower ones or will be equally occupied. To reverse the population ratios and have higher level more occupied than the lower levels, temperatures even higher than infinity are needed. A population ratio larger than one would require T<o or negative. This temperature at which population inversion occurs is called negative absolute temperature. This temperature must be beyond infinity.

To understand the phenomenon of negative absolute temperature, consider a system of 'N' particles existing only in two energy levels. i.e in zero and 1st level. The entropy 'S' when plotted as a function of energy the following curve is obtained.

NOTE



At zero energy all the 'N' particles are in the zero level (lowest) which the state of minimum disorder to minimum entropy is $\left(\frac{\partial S}{\partial E}\right)_{V,N} = 1/T$

As the temperature is increased or energy is supplied to the system population in the upper level increases. When the two energy levels are equally populated the internal energy of the system will correspond to NE/2. There is maximum disorder and maximum entropy. It is the most probable state and ∂S/∂E =1/T =0 as T→∞ or more energy is supplied all the 'N 'particles will be in the upper level. E=N_E. This is a state of maximum energy and minimum entropy with minimum disorder. The left half of the curve has a positive slope i.e $\left(\frac{\partial S}{\partial E}\right) = 1/T$ is positive that is T is +ve. The right half of the curve as negative slope ie $\left(\frac{\partial S}{\partial E}\right) = 1/T$ = -ve that is T= -ve. This is the region of negative absolute temperature. Negative absolute temperatures are defined by the slope of S vs E curves.

In the figure as we proceed from left to right in the direction of increasing energy there is increasing hotness and therefore increase in entropy. At the position of maximum entropy where both the energy levels are equally populated, the temperature is infinite. Beyond the maximum the temperature must be hotter than infinity. Hence negative absolute temperatures are hotter than infinity.

1.4 Check Your Progress

1. What is meant by statistical therrmodynamics?
2. Write the Maxwell – Boltzmann distribution law for the system having N distinguishable particles distributed in non degenerated energy levels.

NOTE

3. Give the expression for Maxwell distribution law of molecular energies.
4. What are the relative populations of the states of a two-level system when the temperature is infinite?
5. What are the relative populations of the states of a two-level system as the temperature approaches zero?

1.5 Answers to Check Your Progress Questions

1. **Statistical thermodynamics** is the study of the microscopic behaviors of thermodynamic systems using probability theory. Statistical thermodynamics, generally, provides a molecular level interpretation of thermodynamic quantities such as work, heat, free energy, and entropy.

2. $n_i = e^{-\alpha}.e^{-\beta E_i} = \exp^{(-\alpha)}.\exp^{(-\beta E_i)}$ is called Maxwell – Boltzmann distribution law for the system having N distinguishable particles distributed in non degenerated energy levels.

3. $n_i = \dfrac{g_i}{e^{\alpha+\beta E_i}} = g_i e^{-\alpha-\beta E_i}$ $\quad (\alpha = \dfrac{-\mu}{RT}, \beta = \dfrac{1}{KT})$

$= g_i e^{+\mu/RT}.e^{-E_i/KT}$

Where, g_i is the degree of degeneracy or statistical weight factor for the i^{th} level. This expression is called Maxwell Boltzmann distribution law.

4. All the molecules will be in the ground state as $T\rightarrow\infty$ $n_i/n_o = 1$ and the population of the states will be equal.

5. At T = 0 ni/no=0.

1.6 Summary

- In thermodynamics, **statistical thermodynamics** is the study of the microscopic behaviors of thermodynamic systems using probability theory. Statistical thermodynamics, generally, provides a molecular level interpretation of

thermodynamic quantities such as work, heat, free energy, and entropy

- Maxwell–Boltzmann statistics gives the average number of particles found in a given single-particle microstate.
- The energies of such particles follow what is known as **Maxwell-Boltzmann** statistics, and the statistical **distribution** of speeds is derived by equating particle energies with kinetic energy.
- One very important conclusion that will emerge from the following analysis is that the populations of states depend on a single parameter, the 'temperature'. That is, statistical thermodynamics provides a molecular justification for the concept of temperature and some insight into this crucially important quantity.

1.7 Keywords

1. . **Statistical thermodynamics** is the study of the microscopic behaviors of thermodynamic systems using probability theory.
2. The weight of a configuration is the number of ways that molecules can be distributed over the available states.
3. The most probable distribution, that of the greatest weight, is the Boltzmann distribution.

1.8 Self-assessment questions and exercises

1. Derive Maxwell distribution law of molecular energies.
2. Explain Negative Kelvin Temperature.

1.9 Further readings

1. **Statistical Thermodynamics**, M.C. Gupta, Wiley Eastern, New Delhi,1990.

2. **Introduction to Statistical Thermodynamics**, R.P.H.Gasser and W.G.Richards, World Scientific, Singapore, 1995.

3. Physical chemistry, Peter Atkins, Julio De Paula, 9th edition, 2010.

Unit- II Partition Function

Structure

2.0 Introduction

In physics,a partition function describes the statistical properties of a system in thermodynamic equilibrium. Partition functions are functions of the thermodynamic state variables, such as the temperature and volume. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives. The partition function is dimensionless, it is a pure number.

Each partition function is constructed to represent a particular statistical ensemble (which, in turn, corresponds to a particular free energy). The most common statistical ensembles have named partition functions. The **canonical partition function** applies to a canonical ensemble, in which the system is allowed to exchange heat with the environment at fixed temperature, volume, and number of particles. The **grand canonical partition function** applies to a grand canonical ensemble, in which the system can exchange both heat and particles with the environment, at fixed temperature, volume, and chemical potential. A a thermodynamically large system is in thermal contact with the environment, with a temperature T,

NOTE

and both the volume of the system and the number of constituent particles are fixed. A collection of this kind of systems comprises an ensemble called a canonical ensemble.

2.1 Objectives

After going through this unit, you will be able to:

- Understand the concept behind Partition function
- Learn about how many Microstates are accessible to your system in a given ensembles
- Explains the thermodynamic functions in terms of partition function
- The physical basis of equilibrium can be understood by using the principles of statistical thermodynamics.

2.2 Partition Function

Quantum theory permits a qualitative explanation of energy, heat capacity and other related thermodynamic quantities for di and polyatomic molecules. A quantitative interpretation is provided by the use of certain general function is called "partition function". Mathematically it was written as

$$q = \sum_{i=0}^{\infty} g_i e^{-E_i/KT}$$

Where 'q' is the molecular partition function

Partition function is derived from Maxwell Boltzmann distribution law. According to Maxwell Boltzmann distribution law

$$n_i = \frac{n_0}{g_0} g_i e^{-E_i^0/KT}$$

Total number of molecules = $N = \sum_{i=0}^{\infty} n_i$

N= $n_o + n_1 + n_2 + n_3 +$ -------n_i + ---

$$N = \frac{n_0}{g_0} g_0 e^{-E_0/KT} + \frac{n_0}{g_0} g_1 e^{-E_1/KT} + \frac{n_0}{g_0} g_2 e^{-E_2/KT} + \ldots\ldots\ldots\ldots + \frac{n_0}{g_0} g_i e^{-E_i/KT} + \ldots\ldots$$

NOTE

$$N = \frac{n_0}{g_0}[g_0 e^{-E_0/KT} + g_1 e^{-E_1/KT} + g_2 e^{-E_2/KT} + \ldots\ldots\ldots\ldots g_i e^{-E_i/KT}\ldots\ldots]$$

$$N = \frac{n_0}{g_0}\sum_{i=0}^{\infty} g_i e^{-E_i/KT}$$

Where $\sum_{i=0}^{\infty} g_i e^{-E_i/KT}$ is called “partition function”. The summation is taken over all integral values of ’i’ from zero to infinity. It is represented by the letter q or z

$$q = \sum_{i=0}^{\infty} g_i e^{-E_i/KT}$$

$$N = \frac{n_0}{g_0}.q \quad q = g_0\frac{N}{n_0} \text{ when } g_0=1,\ q = \frac{N}{n_0}$$

i.e partition function is the ratio of the total number of molecules in the ground state. Again

$$q = g_0\frac{1}{n_0/N} \text{ when } g_0=1,\ q = \frac{1}{n_0/N}$$

Partition function is the reciprocal of the mole fraction of the molecules in the ground state. It is a mere number and is a dimensionless quantity.

$$q = \sum_{i=0}^{\infty} g_i e^{-E_i/KT}$$

Partition function will never be equal to zero. It may vary from unity to infinity. As T→0 q→1(E_o=0).

NOTE

2.2.1 Vibrational Partition Function

Partition function is defined mathematically as

$$q = \sum_{i=0}^{\infty} g_i e^{-E_i/KT}$$

Vibrational partition function is given by

$$q_v = \sum_{v=0}^{\infty} g_v e^{-E_v/KT}$$

Where g_v is the degeneracy factor associated with the vibrational level. It is unity and E_{vib} is the energy of the vibrational state in excess of the zero point energy.

The lowest or ground state energy or zero point energy of simple harmonic oscillators is given by $E_v = 0 = \frac{1}{2}h\nu$; where 'v' is the fundamental frequency of oscillation.

$\nu = \frac{1}{2\pi}\sqrt{K/\mu}$ Where K is the force constant and --- the reduced mass of the system.

The actual value of energy of vibration is given by the expression

$$E_{vib} = (V + \frac{1}{2})h\nu$$

Where, V is the vibrational quantum number. It can take up value from 0 to ∞ and h is the Planck's constant for v=0, $E_v = 0 = \frac{1}{2}h\nu$ which is the zero point energy of the vibrator. Hence energy of the vibrational states in excess of the zero point energy is

$$E_v = (V + \frac{1}{2})h\nu - \frac{1}{2}h\nu = Vh\nu \quad (g_v=1)$$

$$q_v = \sum_{v=0}^{\infty} g_v e^{-E_v/KT} = \sum_{v=0}^{\infty} e^{-vhv/KT}$$

$$q_{vib} = e^{-0hv/KT} + e^{-hv/KT} + e^{-2hv/KT} + e^{-3hv/KT} + \ldots\ldots\ldots\ldots$$

NOTE

$e^o = 0$

$$\text{put } hv/KT = x = 1 + e^{-x} + e^{-2x} + e^{-3x} + \ldots\ldots\ldots\ldots$$

$$q_{vib} = \frac{1}{1-e^{-x}} = \frac{1}{1-e^{-hv/KT}} = \frac{e^{hv/KT}}{e^{(hv/KT)}-1}$$

The series $1 + e^{-x} + e^{-2x} + e^{-3x} +$ converges to

$$\frac{1}{1-e^{-x}} = \frac{1}{1-\frac{1}{e^{+x}}} = \frac{e^x}{e^{+x}-1} = \frac{e^x}{e^x-1}$$

$$q_{vib} = \frac{1}{(1-e^{-hv/KT})} = \frac{1}{(1-e^{-hc\bar{v}/KT})}$$

$\bar{v}$ = wave number of oscillation when zero point energy is also included.

$$q_{vib} = \frac{e^{-hv/2KT}}{1-(e^{-hv/KT})} = \frac{e^{+hv/2KT}}{e^{hv/KT}-1}$$

This expression is used to determine the vibrational partition function of a diatomic molecule at all temperatures provided the vibrational frequency is known. Vibrational frequency is obtained from the study of the spectrum of the molecule.

If $\theta_v = hv/K$, the vibrational characteristic temperature,

$$q_{vib} = 1/1 - e^{-\theta_v/T}$$

1. Greater the value of θ_v ($\theta_v = hv/K$) i.e. higher the value of the vibrational frequency lower will be the vibrational partition function and lesser will be the fraction of the

molecules in the excited vibrational states.

2. Greater the value of greater T will be the value of vibrational partition function.

NOTE

2.2.2 Rotational Partition Function

Partition function is given by the expression

$$q = \sum_{i=0}^{\infty} g_i e^{-E_i/KT}$$

For rotational part of the partition function

$$q_r = \sum_{J=0}^{\infty} g_J e^{-E_J/KT}$$

where g_J is the degeneracy factor or statistical weight factor for the rotational levels and is equal to (2J +1) where J is the rotational quantum number. Ej is the energy of the rotational level in excess of the zero point value.

Rotational energy of the rigid diatomic molecule is obtained by solving the schrodinger wave equation.

$E_J = \frac{J(J+1)h^2}{8\pi^2 I}$; Where J is the rotational quantum number. J can taken up values from 0 to ∞ when J = 0 E_J =0

'h' is the Planck's, constant and I the moment of inertia I =μr^2 where μ is the reduced mass of the system and r, internuclear distance . Greater the value of 'I' lesser will be the value of E_J

Inserting the value of E_J in the expression for partition function, we get

$$q_r = \sum_{J=0}^{\infty} (2J+1) e^{\frac{-J(J+1)h^2}{8\pi^2 IKT}}$$

Provided moment of inertia is moderately large and the temperature not too low for all diatomic molecules except H_2 and D_2 the summation is replaced by integration and hence

NOTE

$$q_r = \sum_{J=0}^{\infty}(2J+1)e^{\frac{-J(J+1)h^2}{8\pi^2 IKT}}$$

Assume $\frac{h^2}{8\pi^2 IK} = \theta_r$ where θ_r is called rotational characteristic temperature

Put $x = \frac{J(J+1)h^2}{8\pi^2 IKT} = \frac{J(J+1)\theta_r}{T}$

$$x.\frac{T}{\theta_r} = J(J+1)$$

$$\frac{T}{\theta_r}.dx = (2J+1)dJ$$

Hence,

$$q_r = \int_0^{\infty}\frac{T}{\theta_r}.e^{-x}dx$$

$$q_r = \frac{T}{\theta_r}.\int_0^{\infty} e^{-x}dx$$

$$q_r = \frac{T}{\theta_r}.1$$

$$q_r = \frac{T}{\frac{h^2}{8\pi^2 IK}} = \frac{8\pi^2 IKT}{h^2}$$

For heteronuclear diatomics

$$q_r = \frac{8\pi^2 IKT}{h^2}$$

For symmetric molecules (like homonuclear diatomic molecule) a factor called symmetry factor represented by the letter σ is introduced in the denominator. Hence in general for all diatomic

molecules.

$$q_r = \frac{8\pi^2 IKT}{\sigma h^2}$$

The symmetry factor σ is the number of a identical indistinguishable configurations a molecule can assume during one complete rotation.

For homonuclear diatomic molecule like H_2O_2, N_2, Cl_2 etc σ =2, for

heteronuclear diatomic molecules like HCl, ICl, CO, NO etc.

σ =1. For linear molecules like CO_2 σ = 2

Interpretation

$$q_r = \frac{8\pi^2 IKT}{\sigma h^2}$$

1. q_r is independent of the volume of the container
2. q_r depends on the symmetry of the molecule, greater the symmetry of the molecule lesser will be the rotational partition function.
3. q_r depends on the moment of inertia and temperature. It is directly proportional to I and T.

2.2.3 Elecronic Partition function

Partition function may be defined mathematically as

$$q = \sum_{i=0}^{\infty} g_i e^{-E_i/KT}$$

Where, g_i is the degeneracy factor for the i^{th} level having energy E_i in excess of the zero point level at temperature T.

NOTE

The electronic partition is given by

$$q_e = \sum_{i=0}^{\infty} (g_e)_i e^{-(E_e)_i/KT}$$

$$q_e = (g_e)_0\, e^{-(E_e)_0/KT} + (g_e)_1\, e^{-(E_e)_1/KT} + (g_e)_2\, e^{-(E_e)_2/KT} + \ldots\ldots\ldots\ldots\ldots\ldots$$

$$q_e = (g_e)_0\, e^{-(E_e)_0/KT}\left(1 + \frac{(g_e)_1}{(g_e)_0} e^{-(E_{e_1}-E_{e_0})/KT} + \frac{(g_e)_2}{(g_e)_0} e^{-(E_{e_2}-E_{e_0})/KT} + \ \right)$$

The energy spacings of the electronic energy levels are very large compared to those of vibrational and rotational levels. For most atoms except chlorine and molecules except O_2, NO and NO_2 the energy of the next higher electronic state is much greater than εe_0 so that $\left(\frac{\varepsilon e_1 - \varepsilon e_0}{KT}\right)$ is very large at moderate temperatures.

Hence second and other terms can be neglected and hence the electronic partition function

$$q_e = (g_e)_0\, e^{-(E_e)_0/KT}$$

The degeneracy or statistical weight factor for the electronic level normal or excited is (2J +1)

In general $q_e = \sum_{e_{i=0}}^{\infty} (g_e)_i e^{-(E_e)_i/KT}$

In the ground state $(Ee)_0$ is zero. Hence $e^{-(E_e)_0/KT} = 1$. The contribution of this state to the electronic partition function is thus (2J +1).

He, Ne, Na vapour, Hg etc have single electronic ground state and for the atoms of these elements the energy difference between the lowest and the next electronic level is very high.

Many monoatomic substances e.g. Cl_2 and a few polyatomic molecules e.g. O_2, NO have multiplet electronic ground states and there may be low lying excited electronic states.

NOTE

Hence one or more electronic states above the ground state are appreciably occupied even at moderate temperatures and hence appropriate terms must be included in the partition function.

Example: the lowest state of chlorine atom having the energy (Ee)o = zero , the value of j is 3/2 and there is another state energy $(Ee)_1 = E_1$ with J value ½ . Hence the electronic partition function q_e at ordinary temperature.

$$q_e = \sum_{e_{i=0}}^{\infty} g_{ei} e^{-(E_e)_i/KT}$$

$$q_e = (g_e)_0 e^{-(E_e)_0/KT} + (g_e)_1 e^{-(E_e)_1/KT}$$

$$(g_e)_0 = (2J+1) = (2 \times \frac{3}{2} + 1) = 4$$

$$J = 3/2$$

$$(g_e)_1 = (2J+1) = (2 \times \frac{1}{2} + 1) = 2$$

$$J = 1/2$$

$$(E_e)_0 = 0 \text{ , } (E_e)_1 = E_1$$

$$q_e = 4 + 2e^{-E_1/KT}$$

where, E_1 is the energy of the upper level in excess of the zero point level.

At higher temperatures other terms would have to be included.

The value of $E_1 = h\nu$ is found from the spectrum of chlorine. Thus

$$(q_e)_{Cl} = 4 + 2e^{-h\nu/KT}$$

$$= 4 + 2e^{-hc\bar{\nu}/KT}$$

Internal energy with respect to electronic motion

$$(Ee)_{Cl} = NKT^2 \left(\frac{\partial \ln q_e}{\partial T}\right)$$

NOTE

$$= NKT^2 \frac{\partial}{\partial T} \ln(4 + 2e^{-hc\bar{v}/KT})$$

$$= R.(\frac{hc\bar{v}}{K}). \frac{1}{(2e^{-hc\bar{v}/KT})+1}$$

$$= (\frac{\partial(E_e)_{Cl}}{\partial T})_V$$

$$= \frac{\partial}{\partial T} (R(hc\bar{v}/R). \frac{1}{2e^{hc\bar{v}/KT}+1})$$

$$= 2R.(\frac{hc\bar{v}}{KT})^2 . \frac{e^{hc\bar{v}/KT}}{2e^{hc\bar{v}/KT}+1})$$

By knowing $\bar{v}$ at a moderate temperature the value of q_e, E_e & $(Cv)_e$ can be evaluated. The possibility of electronic states would fail if applied to atomic chlorine at temperatures, greater than 250K. The higher the temperature the greater is discrepancy.

2.3 Thermodynamic functions in terms of partition function

2.3.1 Internal energy from partition function

Let E be the total energy of N molecules present in the system.
Average energy <E> is given by

$$< E > = \frac{E}{N} = \frac{\sum_{i=0}^{\infty} E_i n_i}{\sum_{i=0}^{\infty} n_i} \longrightarrow (\ )$$

($E = \sum_{i=0}^{\infty} E_i n_i$ $N = \sum_{i=0}^{\infty} n_i$ from postulate (3) and (4) of Maxwell Boltzmann Distribution Law)

Applying Maxwell Boltzmann Distribution Law

i.c $n_i = \frac{n_0}{g_0} g_i e^{-E_i/KT}$ in equation (1)

$$< E >= \frac{\sum_{i=0}^{\infty} E_i \frac{n_0}{g_0} g_i e^{-E_i/KT}}{\sum_{i=0}^{\infty} \frac{n_0}{g_0} g_i e^{-E_i/KT}}$$

$$< E >= \frac{\frac{n_0}{g_0} \sum_{i=0}^{\infty} E_i g_i e^{-E_i/KT}}{\frac{n_0}{g_0} \sum_{i=0}^{\infty} g_i e^{-E_i/KT}} \rightarrow (2)$$

Molar Partition function (Q) is given by

$$Q = \sum_{i=0}^{\infty} g_i e^{-E_i/KT}$$

i.e substituting Q value in equation (2)

$$\text{Hence } < E >= \frac{\sum_{i=0}^{\infty} E_i g_i e^{-E_i/KT}}{Q} \rightarrow (3)$$

$$Q = \sum_{i=0}^{\infty} g_i e^{-E_i/KT}$$

Differentiating 'Q' with respect to temperature at constant volume

$$\left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial}{\partial T} \sum_{i=0}^{\infty} g_i e^{-E_i/KT}\right)_V$$

$$= \sum_{i=0}^{\infty} g_i e^{-E_i/KT} \left(\frac{-E_1^0}{K}\right)\left(\frac{-1}{T^2}\right)$$

$$\left(e^{f(x)} = e^{f(x)}.df(x) \right)$$

$$\left(\frac{\partial Q}{\partial T}\right)_V = \sum_{i=0}^{\infty} \frac{E_i g_i e^{-E_i/KT}}{KT^2}$$

$$KT^2 \left(\frac{\partial Q}{\partial T}\right)_V = \sum_{i=0}^{\infty} E_i g_i e^{-E_i/KT} \rightarrow (4)$$

NOTE

Incorporation of this result in equation (3)

$$< E >= \frac{KT^2 (\frac{\partial Q}{\partial T})_V}{Q} \qquad \frac{1}{Q}(\frac{\partial Q}{\partial T})_V = (\frac{\partial \ln Q}{\partial T})_V$$

$$< E >= KT^2 (\frac{\partial \ln Q}{\partial T})_V$$

Internal energy $E = KT^2 (\frac{\partial \ln Q}{\partial T})_V$

q=molecular Partition function $q^N = Q$

$$E = KT^2 (\frac{\partial \ln q^N}{\partial T})_V$$

$$E = NKT^2 (\frac{\partial \ln q}{\partial T})_V \rightarrow (5)$$

Hence it is possible to determine the internal energy of the system if the partition function is known.

2.3.2 Heat capacity from partition function

$$(\frac{\partial E}{\partial T})_V = C_V$$

substituting E from (5) and simplifying the differential, we get

$$C_V = \frac{\partial}{\partial T} [NKT^2 \frac{\partial \ln q}{\partial T}]_V$$

$$= \frac{NK}{T^2} . \frac{\partial^2 \ln q}{\partial (1/T)^2}$$

.

NOTE

2.3.3 Entropy from partition function

Thermodynamic probability is the numbers of ways in which system consisting of N identical indistinguishable molecules can be realized.

$$W = \prod_{i=0}^{\infty} \frac{g_i^{n_i}}{n_i!}$$

$$\ln W = \ln\left(\prod_{i=0}^{\infty} \frac{g_i^{n_i}}{n_i!}\right)$$

$$= \ln\left(\prod_{i=0}^{\infty} g_i^{n_i}\right) - \ln\left(\prod_{i=0}^{\infty} n_i!\right)$$

$$\ln W = \sum_{i=0}^{\infty} n_i \ln g_i - \sum_{i=0}^{\infty} n_i! \rightarrow (1)$$

Applying stirlings approximation formula in equation (1)

$$\ln N! = N \ln N - N$$

$$\ln W = \sum_{i=0}^{\infty} n_i \ln g_i - \sum_{i=0}^{\infty} (n_i \ln n_i - n_i)$$

$$\ln W = \sum_{i=0}^{\infty} n_i \ln g_i - \sum_{i=0}^{\infty} n_i \ln n_i - n_i + \sum_{i=0}^{\infty} n_i$$

According to Maxwell Boltzmann distribution law

$n_i = \frac{n_0}{g_0} g_i e^{-E_i/KT}$ but $\frac{n_0}{g_0} = \frac{N}{q}$ 'q'-molecular partition function

Hence, $n_i = \frac{N}{q} g_i e^{-E_i/KT}$

$$\ln W = \sum_{i=0}^{\infty} n_i \ln g_i - \sum_{i=0}^{\infty} n_i \ln\left(\frac{N}{q}\right) g_i e^{-E_i/KT} + \sum_{i=0}^{\infty} n_i$$

$$\ln W = \sum_{i=0}^{\infty} n_i \ln g_i - \sum_{i=0}^{\infty} n_i \ln\left(\frac{N}{q}\right) g_i - \sum_{i=0}^{\infty} n_i \ln e^{-E_i/KT} + \sum_{i=0}^{\infty} n_i = 0$$

NOTE

$$\ln W = \sum_{i=0}^{\infty} n_i \ln g_i - \sum_{i=0}^{\infty} n_i \ln \frac{N}{q} - \sum_{i=0}^{\infty} n_i \ln g_i - \sum_{i=0}^{\infty} n_i \ln e^{-E_i/KT} + \sum_{i=0}^{\infty} n_i = 0$$

$$= \sum_{i=0}^{\infty} n_i \ln(\frac{q}{N}) + \frac{n_i E_i}{KT} + N \qquad (\sum_{i=0}^{\infty} n_i = N)$$

(ln and e gets cancelled, by postulate (3) of Maxwell Boltzmann distribution law)

$$\ln W = \sum_{i=0} n_i \ln(\frac{q}{N}) + \frac{E}{KT} + N \qquad ((n_i E_i = E) \text{ by postulate (4) of}$$

Maxwell Boltzmann distribution law

$$\ln W = N \ln q - N \ln N + \frac{E}{KT} + N$$

$$= N \ln q - (N \ln N) - N + \frac{E}{KT}$$

$$\ln W = \ln q^N - \ln(N!) + \frac{E}{KT}$$

$$\ln W = \ln(\frac{q^N}{N!}) + \frac{E}{KT}$$

Multiplying throughout by K

$$K \ln W = S = K \ln(\frac{q^N}{N!}) + \frac{KE}{KT}$$

$(\therefore S = K \ln W)$ (Boltzmann-Plank entropy probability law)

We know that internal energy

$$E = NKT^2 (\frac{\partial \ln q}{\partial T})_V$$

$$E = KT^2 (\frac{\partial \ln q^N}{\partial T})_V$$

$$E = KT^2 (\frac{\partial \ln Q}{\partial T})_V$$

$\frac{q^N}{N!} = Q$ for identical indistinguishable particles

NOTE

i.e. equation (2) becomes

$$S = K \ln Q + \frac{KT^2}{T}\left(\frac{\partial \ln Q}{\partial T}\right)_V$$

$$S_{molar} = K \ln Q + KT\left(\frac{\partial \ln Q}{\partial T}\right)_V$$

Molar entropy of an ideal gas can be determined from the knowledge of partition function.

2.3.4 Pressure from partition function

$$dA = -PdV - SdT$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_V = -\left(\frac{\partial A}{\partial Q}\right)_T\left(\frac{\partial Q}{\partial V}\right)_T \rightarrow (1)$$

Since Helmholtz free energy

$$A = -KT \ln Q \qquad \left(\ln Q = \frac{1}{Q}\right)$$

$$\left(\frac{\partial A}{\partial Q}\right)_T = \frac{-KT}{Q} \rightarrow (2)$$

Substituting (2) in equation (1), we get

$$P = \frac{KT}{Q}\left(\frac{\partial Q}{\partial V}\right)_T \quad \text{(or)} \quad \frac{1}{Q}\left(\frac{\partial Q}{\partial T}\right)_T = \left(\frac{\partial \ln Q}{\partial T}\right)_V$$

$$P = KT\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

.

2.3.5 Third law and partion function

Internal energy E of a system is a function of T and V.

$$E = f(T, V)$$

Applying rules of partial differentiation,

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \rightarrow (1)$$

NOTE

from the combined 1st and 2nd law of thermodynamics.

$$dE = q - W$$

$$dE = TdS - PdV$$

$$TdS = dE + PdV \rightarrow (2)$$

Substituting the value of dE from equation (1) in equation (2), we get

$$TdS = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV \rightarrow (3)$$

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V$$

At constant volume dV=0, i.e. equation (3) becomes

$$TdS = C_V dT$$

$$dS = C_V \frac{dT}{T}$$

Entropy change for a finite process

$$\int_{S_0}^{S_T} dS = \int_0^T C_V \frac{dT}{T}$$

$$S_T - S_0 = \int_0^T \frac{1}{T} \cdot \left(\frac{\partial E}{\partial T}\right)_V dT \qquad E = KT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_v dT$$

$$S_T - S_0 = \int_0^T \frac{1}{T} \frac{\partial}{\partial T} \left(KT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V\right) dT$$

$$S_T - S_0 = \int_0^T \frac{1}{T} \partial KT^2 \left(\frac{\partial \ln Q}{\partial T}\right) \qquad \int UdV = UV - \int VdU$$

NOTE

$$= \frac{1}{T} KT^2 (\frac{\partial \ln Q}{\partial T})_V - \int_0^T KT^2 (\frac{\partial \ln Q}{\partial T})_V (-\frac{1}{T^2}) dT$$

$$= KT (\frac{\partial \ln Q}{\partial T})_V + \int_0^T K\partial \ln Q$$

$$S_T - S_0 = KT (\frac{\partial \ln Q}{\partial T})_V + [K \ln Q]_0^T$$

$$S_T - S_0 = KT (\frac{\partial \ln Q}{\partial T})_V + K \ln Q_{T=T} - K \ln Q_{T=0}$$

Comparing left and right hand sides and equating the temperature dependent and temperature independent terms we get

$$S_T = KT (\frac{\partial \ln Q}{\partial T})_V + K \ln Q_{T=T}$$

$$S_0 = K \ln Q_{T=0}$$

When T=0, Q=1 hence KlnQ=0

This is 3rd law i.e. All perfect crystalline solids at 0^oK will have zero entropy

2.3.6 Helmholtz Free Energy from Partition Fuction

Helmholtz free energy is A = -KTlnQ

According to thermodynamic eqn

$$A = E - TS$$

Substituting the expressions for E and S in terms of partition function

$$E = KT^2 (\frac{\partial \ln Q}{\partial T})_V \quad \text{(from internal energy)}$$

$$S = K \ln Q + KT (\frac{\partial \ln Q}{\partial T})_V \quad \text{(from entropy)}$$

$$A = KT^2 (\frac{\partial \ln Q}{\partial T})_V - T (K \ln Q + KT (\frac{\partial \ln Q}{\partial T})_V)$$

$$A = KT^2 (\frac{\partial \ln Q}{\partial T})_V - KT \ln Q - KT^2 (\frac{\partial \ln Q}{\partial T})_V)$$

$$A = -KT \ln Q$$

2.3.7 Enthalpy from partion function

NOTE

$$H = E + PV$$

$$E = KT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V \quad \text{(From internal energy)}$$

$$P = KT \left(\frac{\partial \ln Q}{\partial T}\right)_T \quad \text{(From pressure)}$$

$$H = KT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V + KT \left(\frac{\partial \ln Q}{\partial V}\right)_T .V$$

$$= KT[T.\left(\frac{\partial \ln Q}{\partial T}\right)_V + V \left(\frac{\partial \ln Q}{\partial V}\right)_T]$$

$$H = KT[\frac{\partial \ln Q}{\partial T/T} + \frac{\partial \ln Q}{\partial V/V}]$$

$$H = KT[\frac{\partial \ln Q}{\partial \ln T} + \frac{\partial \ln Q}{\partial \ln V}]$$

2.3.8 Gibbs free energy from partition function

$$G = H - TS$$

$$= E + PV - TS$$

$$G = A + PV$$

$$A = -KT \ln Q$$

$$P = KT \left(\frac{\partial \ln Q}{\partial T}\right)_T$$

$$G = -KT \ln Q + KT \left(\frac{\partial \ln Q}{\partial T}\right)_T .V$$

$$G = KT[\left(\frac{\partial \ln Q}{\partial \ln V}\right)_T - \ln Q]$$

2.6 Check Your Progress

1. Define partion function.
2. Define canonical ensemples
3. Give an expersssion for Helmholtz free energy from partition function.
4. Give the σ value (symmetry factor) for H_2O_2, HCl, CO_2.

2.7 Answers to check your progress questions

1. partition function describes the statistical properties of a system in thermodynamic equilibrium. Partition functions are functions of the thermodynamic state variables, such as the temperature and volume.

   Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives. The partition function is dimensionless, it is a pure number.

A quantitative interpretation is provided by the use of certain general function is called "partition function". Mathematically it was written as

$$q = \sum_{i=0}^{\infty} g_i e^{-E_i / KT}$$

Where 'q' is the molecular partition function

2. A a thermodynamically large system is in thermal contact with the environment, with a temperature *T*, and both the volume of the system and the number of constituent particles are fixed. A collection of this kind of systems comprises an ensemble called a canonical ensemble.
3. $A = -KT \ln Q$
4. σ values for H_2O_2, HCl, CO_2 – 2, 1, 2.

2.8 Summary

- The molecular partition function indicates the number of thermally accessiblestates of a collection of molecules at a temperature *T*.
- The translational partition function is calculated by noting that translational states form a near continuum. When the energy is a sum of contributions from independent modes of motion, the partition function is a product of partition functions for each mode of motion.
- The internal energy is proportional to the derivative of the partition function with respect to temperature.

NOTE

- The parameter $\beta = 1/kT$.
- The statistical entropy is defined by the Boltzmann formula but may be expressed in terms of the molecular partition function.
- A canonical ensemble is an imaginary collection of replications of the actual system with a common temperature. It is used to extend statistical thermodynamics to include interacting molecules.
- The thermodynamic limit is reached when the number of replications becomes infinite.
- Most members of the ensemble have an energy very close to the mean value.
- The internal energy of a system composed of interacting molecules is proportional to the derivative of the canonical partition function with respect to temperature.
- The entropy of an interacting system can be calculated from the canonical partition function.

2.9 Keywords

1. The molecular partition function indicates the number of thermally accessiblestates of a collection of molecules at a temperature *T*.
2. A canonical ensemble is an imaginary collection of replications of the actual system with a common temperature. It is used to extend statistical thermodynamics to include interacting molecules.

3. The thermodynamic information in partition function

a) The internal energy of a system composed of interacting molecules is proportional to the derivative of the canonical partition function with respect to temperature.

b) The entropy of an interacting system can be calculated from the canonical partition function.

The following functions are written in terms of the canonical partition function:

(a) Helmoltz energy,
(b) Pressure,
(c) Enthalpy,
(d) Gibbs energy.

4. The molecular partition function factorizes into a product of:

a) translational,
b) rotational,
c) vibrational, and
d) electronic contributions.

The contributions to the overall partition function are summarized

NOTE

2.10 Self-assessment questions and exercises

1. Define Molecular partition function and ensembles.
2. Define partition function and thermodynamic functions interms of partition function.

2.11 Further readings

1. **Statistical Thermodynamics**, M.C. Gupta, Wiley Eastern, New Delhi,1990.

2. **Introduction to Statistical Thermodynamics**, R.P.H.Gasser and W.G.Richards, World Scientific, Singapore, 1995.

3. **Physical chemistry**, Peter Atkins, Julio De Paula, 9^{th} edition, 2010

UNIT- III statistical interpretation of third law

Structure

3.0 Introduction

The Third law of thermodynamics is sometimes stated as follows, regarding the properties of closed systems in thermodynamic equilibrium:

The entropy of a system approaches a constant value as its temperature approaches absolute zero.

This constant value cannot depend on any other parameters characterizing the closed system, such as pressure or applied magnetic field. At absolute zero (zero kelvin) the system must be in a state with the minimum possible energy. Entropy is related to the number of accessible microstates, and there is typically one unique state (called the ground state) with minimum energy.[1] In such a case, the entropy at absolute zero will be exactly zero. If the system does not have a well-defined order (if its order is glassy, for example), then there may remain some finite entropy as the system is brought to very low temperatures, either because the system becomes locked into a configuration with non-minimal energy or because the minimum energy state is non- unique. The constant value is called the residual entropy of the system.[2] The entropy is essentially a state-function meaning the inherent value of different atoms, molecules, and other configurations of particles including subatomic or atomic material is defined by entropy, which can be discovered near 0 K. The Nernst–Simon statement of the third law of thermodynamics concerns thermodynamic processes at a fixed, low temperature:

The entropy change associated with any condensed system undergoing a reversible isothermal process approaches zero as the temperature at which it is performed approaches 0 K.

Here a condensed system refers to liquids and solids. A classical formulation by Nernst (actually a consequence of the Third Law) is:

It is impossible for any process, no matter how idealized, to reduce the entropy of a system to its absolute-zero value in a finite number of operations.

There also exists a formulation of the Third Law which approaches the subject by postulating a specific energy behavior:

If the composite of two thermodynamic systems constitutes an isolated system, then any energy exchange in any form between those two systems is bounded

3.1 Objectives

After going through this unit, you will be able to:

- Explain about statistical interpretation of third law
- Understand the concept of Bose Einstein distribution law and it's applications
- Understand the concept of Ferrmi Dirac distribution law and it's application.

3.2 Bose Einstein distribution law

The statistics applicable to particles whose total wave function is completely symmetric is known as Bose – Einstein distribution law. Bose Einstein statistics is applicable to Bosons, which are particles with integral spins. i.e 0,1,2,3,4--- ex:photons, $_2{}^4He$, ^2H, ^{14}N, ^{16}O, CO_2 etc. In the statistics thermodynamic probability is the number of ways in which the (n_i) indistinguishable particles can be placed in distinguishable boxes or energy levels (gi) without limiting the number of particles placed in each box or energy level.

$$W = \pi_{i=0}^{\infty} \frac{(g_i - 1 + n_i)!}{(g_i - 1)! n_i !}$$

Where W is the total probability, n_i is the number of particles in the i^{th} level having the degeneracy gi.

Consider a system of N particles of an ideal gas, which are

identical, independent and indistinguishable let n_o particles have energy E_o.

n_1 particles are in the energy state E_1.

n_2 particles are in the energy state E_2

.

.

.

.

n_3 particles are in the energy state E_i.

Such that $\sum_{i=0}^{\infty} n_i = N$ and

$$\sum_{i=0}^{\infty} E_i n_i = E$$

Total number of particles in the system is constant and hence there is no variation in the total number of particles.

$\partial N = 0$ i.e

$$\sum_{i=0}^{\infty} E_i \partial n_i = 0 \rightarrow (1)$$

Total energy of the system is constant

$\partial E = 0$ i.e

$$\sum_{i=0}^{\infty} E_i \partial n_i = 0 \rightarrow (2)$$

Equations 1 and 2 are the two conditions of constraint for a system of gas in statistical equilibrium.

Maximization of thermodynamic probability

According to Bose – Einstein statistics thermodynamic probability is the number of ways in which the system of (n_i) identical indistinguishable particles can be placed in different energy levels (g_i) without any limitation to the occupation number is

$$W = \pi_{i=0}^{\infty} \frac{(g_i - 1 + n_i)!}{(g_i - 1)! n_i !}$$

Where n_i is the number of particles in the i^{th} level having

the degeneracy gi and gi>>ni

Since g_i is very large (g_i >>1) one can be neglected and hence

$$W = \pi_{i=0}^{\infty} \frac{(g_i + n_i)!}{g_i!n_i!}$$

$$\ln W = \ln(\pi_{i=0}^{\infty} \frac{(g_i + n_i)!}{g_i!n_i!})$$

$$\ln W = \sum_{i=0}^{\infty} \ln(g_i + n_i)! - \sum_{i=0}^{\infty} \ln(g_i)! - \sum_{i=0}^{\infty} \ln(n_i)!$$

On using stirlings approximation for factorials of large numbers.

$$\ln W = \sum_{i=0}^{\infty} [(g_i + n_i)\ln(g_i + n_i) - (g_i + n_i)] - \sum_{i=0}^{\infty} (g_i \ln g_i - g_i) - \sum_{i=0}^{\infty} (n_i \ln n_i - n_i)$$

$$\ln W = \sum_{i=0}^{\infty} (g_i + n_i)\ln(g_i + n_i) - \sum_{i=0}^{\infty} g_i - \sum_{i=0}^{\infty} n_i - \sum_{i=0}^{\infty} g_i \ln g_i + \sum_{i=0}^{\infty} g_i - \sum_{i=0}^{\infty} n_i \ln n_i + \sum_{i=0}^{\infty} n_i$$

$$= \sum_{i=0}^{\infty} (g_i + n_i)\ln(g_i + n_i) - \sum_{i=0}^{\infty} g_i \ln g_i - \sum_{i=0}^{\infty} n_i \ln n_i$$

For a system which has attained statistical equilibrium there will be most probable distribution of molecules and the thermodynamic probability of the system will be maximum and hence,

$$\partial W = 0 \textbf{ (or) } \partial \ln W = 0$$

$$\partial \ln W = \sum_{i=0}^{\infty} (g_i + n_i)\frac{1}{(g_i + n_i)} + \sum_{i=0}^{\infty} \ln(g_i + n_i)\partial n_i - 0 - \sum_{i=0}^{\infty} (n_i \times \frac{1}{n_i} + \ln n_i)\partial n_i = 0$$

Unit – 3
Statistical Interpretation of Third Law

NOTE

$$= \sum_{i=0}^{\infty}(1+\ln(g_i+n_i))\partial n_i - \sum_{i=0}^{\infty}(1+\ln n_i)\partial n_i = 0$$

$$\partial \ln W = \sum_{i=0}^{\infty}\ln\left(\frac{g_i+n_i}{n_i}\right)\partial n_i = 0$$

$$\partial \ln W = \sum_{i=0}^{\infty}\ln\left(1+\frac{g_i}{n_i}\right)\partial n_i = 0$$

$$\partial \ln W = -\sum_{i=0}^{\infty}\ln\left(1+\frac{g_i}{n_i}\right)\partial n_i = 0 \rightarrow (3)$$

Equation (3) is the third condition of constraint.

Since there is more than one constraint in the system Larangian method of undetermined multiplier is applied to solve the problem.

Equation (1) multiplied by α, (2) by β and combined with equation (3), we get

$$\alpha\sum_{i=0}^{\infty}\partial n_i + \beta\sum_{i=0}^{\infty}E_i\,\partial n_i - \sum_{i=0}^{\infty}\ln\left(1+\frac{g_i}{n_i}\right)\partial n_i = 0$$

Where α &β are the lagrangian undetermined multipliers.

$$\sum_{i=0}^{\infty}\left(\alpha+\beta E_i - \ln\left(1+\frac{g_i}{n_i}\right)\partial n_i\right) = 0$$

∂n_i's will vary independently and hence $\partial n_i \neq 0$ and coefficient of ∂n_i must be equal to zero.

$$\alpha+\beta E_i - \ln\left(1+\frac{g_i}{n_i}\right) = 0$$

$$\ln\left(1+\frac{g_i}{n_i}\right) = \alpha+\beta E_i$$

$$1+\frac{g_i}{n_i} = e^{\alpha+\beta E_i}$$

$$\frac{g_i}{n_i} = (e^{\alpha+\beta E_i})-1$$

$$n_i = \frac{g_i}{(e^{\alpha+\beta E_i})-1} \qquad \alpha = -\mu/RT \quad \beta = 1/kT$$

$$n_i = \frac{g_i}{(e^{-\mu/RT + E_i/kT}) - 1}$$

As T→∞ $e^{\alpha+\beta E_i}$ >>1 and hence '1' in the denominator can be neglected to get Maxwell Boltzmann distribution law. At low temperatures and for problems concerned with radiation '1' in the denominator cannot be neglected.

NOTE

Applications

1. Bose Einstein distribution law is useful to determine the number of identical and indistinguishable particle in the i^{th} level having the degeneracy g_i with energy E_i excess of the zero of the zero point level.
2. It is used to explain the behavior of Helium at low temperature through Bose – Einstein condensation.
3. It is used to explain the radiation by considering them as photons. It is used to derive Planck's Black body radiation law and all the classical laws of black body radiation.

3.2.1 Photon Gas – Application of Bose – Einstein Distribution Law

3.2.1.1Derivation of Planck's Black Body radiation law

According to Bose-Einstein Distribution law the number of identical indistinguishable particles n_i having the specified energy E_i in excess of zero point energy is

$$n_i = \frac{g_i}{(e^{\alpha+\beta E_i}) - 1} \rightarrow (1)$$

Where, 'g_i' is the degeneracy factor of the translational levels.

Electromagnetic radiations consist of discrete energy particles called photons contained in a container of volume v with a definite energy. Photons do not interact with each other and hence a very small black body is assumed to the present in the container to absorb and emit photons and thus thermal equilibrium is possible. Gibbs free energy of radiation is zero at equilibrium and hence μ = 0 and $\alpha = -\mu/RT = 0$.

NOTE

For this system Bose Einstein distribution law i.e. equation (1) becomes.

$$n_i = \frac{g_i}{e^{\beta E_i} - 1} \rightarrow (2)$$

($\alpha = -\mu/RT = 0$)

dg_i, the degeneracy of the translational states is equal to the number of lattice points contained in 1/8th of the spherical shell of radius n and thickness d_n . the number of lattice points corresponding to the specified energy range us given by 1/8th the volume of the spherical shell of radius n and thickness dn.

$$dg = \frac{4\pi n^2 dn}{8} = \frac{\pi n^2 dn}{2} \rightarrow (3)$$

The length 'l' of the box is related to the wavelength of the de-Broglie wave in particle of one dimensional box as

$$l = n\,\lambda/2 = v^{1\ 3}$$

$$n = \frac{2v^{1/3}}{\lambda} = \frac{2v^{1/3}\gamma}{c} \qquad \because \lambda = c/\gamma$$

$$n^3 = \frac{2^3\, v\gamma^3}{c^3}$$

$$3n^2 dn = \frac{2^3 v 3\gamma^2}{c^3} d\gamma \Rightarrow n^2 dn = \frac{8v\gamma^2 d\gamma}{c^3}$$

Substituting the value of n^2dn in equation (3)

$$dg = \frac{\pi}{2}\frac{8v\gamma^2 d\gamma}{c^3} \rightarrow (4)$$

Radiations are polarized in two ways (i.e. equation (4) ×2)

Hence, $dg = 2.\frac{\pi}{2}.\frac{8v\gamma^2 d\gamma}{c^3}$

$$dg = \frac{8\pi v}{c^3}.\gamma^2 d\gamma \rightarrow (5)$$

Replacing gi, by dg_i and n_i by dn_i and substituting dg value (5) in equation (2) we get

$$dN = \frac{8\pi v}{c^3}.\frac{\gamma^2 d\gamma}{((e^{\beta E_i})-1}$$

'dN' is the number of photons in the energy range from v and v+dv. To obtain the total energy in the range v and v+dv, dN is multiplied by hv, which is the energy of one photon.

$$dE = h\gamma.dn$$

$$dE = h\gamma.\frac{8\pi v}{c^3}.\frac{\gamma^2 d\gamma}{((e^{\beta E_i})-1} = E\gamma d\gamma$$

Energy density=energy per unit volume.

$$dn = \frac{dE}{v} = \frac{8\pi h\gamma^3 d\gamma}{c^3(e^{\beta\varepsilon_i}-1)}$$

$$\frac{dE}{v} = \frac{8\pi h\gamma^3 d\gamma}{c^3(e^{\beta\varepsilon_i KT}-1)} = E_\gamma.d\gamma$$

This is Planck's radiation law in terms of frequency conversion in terms of λ.

$$\gamma = c/\lambda$$

$$\gamma^4 = \frac{c^4}{\lambda^4}$$

$$4\gamma^3 d\gamma = c^4.-4\lambda^{-5} d\lambda$$

$$\gamma^3 d\gamma = \frac{c^4}{\lambda^5}.d\lambda$$

$$d\mu = \frac{8\pi hc^4 d\lambda}{c^3.\lambda^5(e^{hc/\lambda KT}-1)}$$

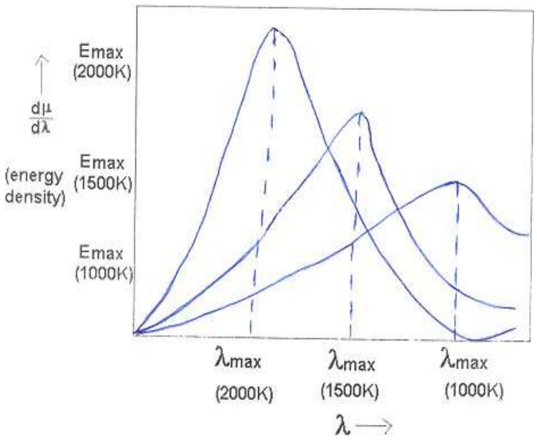
$$d\mu = \frac{8\pi hc}{\lambda^5}.\frac{d\lambda}{(e^{hc/\lambda KT}-1)}$$

$$d\mu = E_\lambda d\lambda$$

NOTE

This expression is Planck's radiation law expressed in terms of wavelength.

When energy density is plotted as a function of λ, the following graph is obtained.



Experimental observation

1. Energy is not distributed uniformly throughout the spectrum.

2. Energy density is minimum both as $\lambda \rightarrow 0$ & $\lambda \rightarrow \infty$. It increases as λ increases, attains a maximum then decreases. The wavelength at which energy density is maximum is called λ_{max} and the maximum energy density corresponding to λ_{max} is called E_{max}.

E_{max} increases with increase in temperature and λ_{max} decreases with increase in temperature.

3. Total energy density increases with increase in temperature.

All the experimental observation is explained by Planck's radiation law.

3.3 Fermi – Dirac Distribution Law

Need for Fermi – Dirac distribution law

1. Maxwell Boltzmann distribution law fails to explain the low temperature behavior of helium and the spectrum of black – body radiation.
2. It does not explain the properties of "electron gas" in metals.
3. It fails to explain the behavior of ideal gas containing identical indistinguishable molecules.

Derivation of Fermi-dirac distribution law

Consider a system of N identical independent indistinguishable particles of an ideal gas. Let there be n_o particles in the energy state E_o, n_1 particles in the energy state E_1, n_2 particles in the energy state E_2 and so on.

1. Total number of particles $\sum_{i=0}^{\infty} n_i = N$

Since the total number of particles in the system is constant.

$$\sum_{i=0}^{\infty} \partial n_i = 0 \rightarrow (1)$$

This is the first condition of constraint.

2 Total energy of the system is constant

$$\sum_{i=0}^{\infty} E_i \partial n_i = 0 \rightarrow (2)$$

This is the second condition of constraint.

Maximization of thermodynamic probability

According to Fermi- dirac statistics the thermodynamic probability or the number of ways in which n_i identical indistinguishable particles can be distributed among g_i energy levels of energy E_i . Such that not more than one particle can occupy a given level is given by

$$W_i = \frac{g_i!}{(g_i - n_i)!n_i!}$$

The total number of ways for the whole system consisting of N particles would be

$$\prod_{i=0}^{\infty} W_i = W = \prod_{i=0}^{\infty} \frac{g_i!}{(g_i - n_i)!n_i!}$$

$$\ln W = \ln \prod_{i=0}^{\infty} \frac{g_i!}{(g_i - n_i)!n_i!} \rightarrow (a)$$

Applying stirlings approximation formula in equation (a)

$$\ln W = \ln \prod_{i=0}^{\infty} g_i! - \ln \prod_{i=0}^{\infty} (g_i - n_i)! - \ln \prod_{i=0}^{\infty} n_i!$$

$$\ln W = \sum_{i=0}^{\infty} \ln g_i! - \sum_{i=0}^{\infty} \ln (g_i - n_i)! - \sum_{i=0}^{\infty} \ln n_i!$$

$$\ln N! = N \ln N - N$$

$$\ln W = \sum_{i=0}^{\infty} g_i \ln g_i - \sum_{i=0}^{\infty} (g_i - n_i) \ln (g_i - n_i) - \sum_{i=0}^{\infty} n_i \ln n_i$$

For a system in statistical equilibrium thermodynamic probability must be maximum. Hence maximization of thermodynamic probability must be maximum. Hence maximization of thermodynamic probability leads to $\partial \ln W = 0$

$$\partial \ln W = 0 - \sum_{i=0}^{\infty} (g_i n_i . \frac{1}{g_i n_i} \partial n_i + \ln(g_i - n_i) \partial n_i) - \sum_{i=0}^{\infty} (n_i . \frac{1}{n_i} \partial n_i + \ln n_i \partial n_i) = 0$$

$$= -\sum_{i=0}^{\infty} (1 + \ln(g_i - n_i)) \partial n_i - \sum_{i=0}^{\infty} (1 + \ln n_i) \partial n_i = 0$$

$$= -\sum_{i=0} \ln(\frac{g_i - n_i}{n_i}) \partial n_i = 0$$

$$= -\sum_{i=0} \ln(\frac{g_i}{n_i} - 1) \partial n_i = 0 \rightarrow (3)$$

This is the third condition of constraint. In order to solve the problem for the system consisting of two or more conditions of constraint Lagrangian method of undetermined multipliers used.

Equation (1) is multiplied by α and equation (2) by β and combined with the condition (3), α and β are the lagrangian undetermined multipliers.

$$\alpha \sum_{i=0}^{\infty} \partial n_i + \beta \sum_{i=0}^{\infty} E_i \, \partial n_i - \sum_{i=0} \ln\left(\frac{g_i}{n_i} - 1\right) \partial n_i = 0$$

$$\sum_{i=0}^{\infty} \left(\alpha + \beta E_i - \ln\left(\frac{g_i}{n_i} - 1\right)\right) \partial n_i = 0$$

Since ∂n_i's can vary independently $\partial n_i \neq 0$ and hence

$$\alpha + \beta E_i - \ln\left(\frac{g_i}{n_i} - 1\right) = 0$$

$$\ln\left(\frac{g_i}{n_i} - 1\right) = \alpha + \beta E_i$$

$$\frac{g_i}{n_i} - 1 = e^{(\alpha + \beta E_i)}$$

$$\frac{g_i}{n_i} = e^{(\alpha + \beta E_i)} + 1$$

$$n_i = \frac{g_i}{e^{(\alpha + \beta E_i)} + 1} \rightarrow (4)$$

$$n_i = \frac{g_i}{e^{(-\mu/RT + E_i/KT)} + 1}$$

Equation (4) is the mathematical expression of Fermi-Dirac distribution law.

Application

1. It is applied to explain the behaviour of "electron gas" in metals and thermionic emission and semiconductors.
2. It helps to determine the number of particles in the i^{th} state with degeneracy g_i, having energy E_i in excess of zero point energy.

3.3.1 Electron Gas – Application of Fermi-Dirac Distribution Law

3.3.1.1 Determination of Average Energy of Free Electron Metals

A metal, each of whose atoms contribute one or more free conducting electrons is regarded as "electron gas".

The number of electrons having energy in the range between E and E+dE is given by Fermi-Dirac distribution law.

$$dN = \frac{dg}{e^{\frac{E_i - E_f}{KT}} + 1}$$

The number of energy levels in the range between E and E+dE for electron in a box of volume is twice that for particles in a box of volume is twice that for particles in a box of volume V because electrons have spin of +1/2 or -1/2. So for electrons,

$$dg = 2 \times \frac{\pi n^2 dn}{2} = \pi n^2 dn \rightarrow (1)$$

$$E = \frac{n^2 h^2}{8ma^2} \quad (a^3 = v, \; a^2 = v^{2/3})$$

$$n^2 = \frac{8mv^{2/3}E}{h^2}$$

$$n = \frac{(8m)^{1/2} V^{1/3} E^{1/2}}{h}$$

$$n^3 = \frac{(8m)^{3/2} V E^{3/2}}{h^3}$$

$$3n^2 dn = \frac{(8m)^{3/2}}{h^3} . V . 3/2 \, E^{1/2} dE$$

Substituting the value of n^2dn in equation (1), we get

$$dg = \frac{\pi (8m)^{3/2}}{2h^3} . V . E^{1/2} dE$$

Hence,

$$dN = \frac{(8m)^{3/2}.\pi.V.E^{1/2}dE}{2h^3.(e^{\frac{E_i-E_F}{KT}}+1)}$$

$$\frac{dN}{dE} = \frac{(8m)^{3/2}.\pi.V.E^{1/2}}{2h^3.(e^{\frac{E_i-E_F}{KT}}+1)}$$

This equation is called Fermi – Dirac formula of free electrons. This represents energy distribution for free electrons.

At absolute zero (i.e. T=O). The particles occupy the lowest level upto E_F, Fermi energy. Fermi energy indicates the maximum energy of fermions in the system.

If there are N electrons in the metal at absolute zero and if the maximum energy of an e^{-n} is EFo is for $O<E_i<EF_o$

$$N = \int dN = \int_0^{EF_0} \frac{(8m)^{3/2}.\pi V}{2h^3.(e^{\frac{E_i-E_F}{KT}}+1)}.dE$$

At absolute zero when $E_i < EF_o$

$$\int dN = N = \int_0^{EF_0} \frac{(8m)^{3/2}.\pi.V}{2h^3}.dE$$

$$N = \frac{(8m)^{3/2}.\pi.V.EF_0^{3/2}}{2h^3 \quad 3/2}$$

$$EF_0^{3/2} = \frac{3Nh^3}{(8m)^{3/2}.\pi V}$$

$$= \frac{3N}{\pi V} \times \frac{h^3}{(8m)^{3/2}}$$

$$EF_0 = \left(\frac{3N}{\pi V}\right)^{2/3} \times \left(\frac{h^3}{(8m)^{3/2}}\right)^{2/3}$$

$$EF_0 = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} = \frac{h^2}{8m}\left(\frac{3}{\pi}.p\right)^{2/3}$$

N/V is the number of free electrons per unit volume. It is the free electron density (ρ). Fermi energy for free electrons in metals can be calculated by knowing the free electron density.

3.4 Check Your Progress

1. What is the third law of thermodynamics?
2. What is the need of Fermi Dirac distribution law?
3. Give the applications of Bose Einstein law.
4. Give the applications of Fermi Dirac distribution law

3.5 Answers to Check Your Progress Questions

1. Third law of Thermodynamics

- The third law of thermodynamics is sometimes stated as follows, regarding the properties of closed systems in thermodynamic equilibrium.

- Here a condensed system refers to liquids and solids. A classical formulation by Nernst (actually a consequence of the Third Law) is:

- It is impossible for any process, no matter how idealized, to reduce the entropy of a system to its absolute-zero value in a finite number of operations.

- There also exists a formulation of the Third Law which approaches the subject by postulating a specific energy behavior:

- If the composite of two thermodynamic systems constitutes an isolated system, then any energy exchange in any form between those two systems is bounded.

2. Need for Fermi Dirac distribution law

- Maxwell Boltzmann distribution law fails to explain the low temperature behavior of helium and the spectrum of black – body radiation.
- It does not explain the properties of “electron gas” in metals.
- It fails to explain the behavior of ideal gas containing identical indistinguishable molecules.

3. Applications of Bose Einstein distribution law

- Bose Einstein distribution law is useful to determine the number of identical and indistinguishable particle in the i^{th} level having the degeneracy g_i with energy E_i excess of the zero of the zero point level.
- It is used to explain the behavior of Helium at low temperature through Bose – Einstein condensation.
- It is used to explain the radiation by considering them as photons. It is used to derive Planck's Black body radiation law and all the classical laws of black body radiation.

4. Fermi Dirac distribution law

- It is applied to explain the behaviour of "electron gas" in metals and thermionic emission and semiconductors.
- It helps to determine the number of particles in the i^{th} state with degeneracy g_i, having energy E_i in excess of zero point energy.

3.6 Summary

- **Bose–Einstein statistics** describe one of two possible ways in which a collection of non-interacting, indistinguishable particles may occupy a set of available discrete energy states at thermodynamic equilibrium.
- The Bose–Einstein statistics apply only to those particles not limited to single occupancy of the same state—that is, particles that do not obey the Pauli exclusion principle restrictions. Such particles have integer values of spin and are named bosons, after the statistics that correctly describe their behaviour. There must also be no significant interaction between the particles.
- Fermi–Dirac and Bose–Einstein statistics apply when quantum effects are important and the particles are "indistinguishable". Quantum effects appear if the concentration of particles satisfies
- Fermi–Dirac statistics apply to fermions (particles that obey the Pauli exclusion principle), and Bose–Einstein statistics apply to bosons.. Both Fermi–Dirac and Bose–Einstein become Maxwell–Boltzmann statistics at high temperature or at low concentration.

3.7 Keywords

The Bose Einstein distribution describes the statistical behaviour integer spin particles (bosons). At low temperature, bosons can behave very differently than fermions because an unlimited number of them can collect into the same energy state, a phenomenon called "condensation".

The Fermi Dirac distribution function, also called Fermi function, provides the probability of occupancy of energy levels by fermions. Fermions are half – integer spin particles, which obey the Pauli exclusion principle. The

NOTE

Pauli exclusion principle postulatestht only one fermion can occupy a single quantum state.

3.8 Self-Assessment Questions and Exercises

1. Derive Bose Einstein distribution law and give its applications.
2. Derive Plank's black body radiation law using Bose Einstein distribution law.
3. Derive Fermi Dirac distribution law and give its applications.
4. Determind the average energy of free electron metals using Ferrmi Dirac distribution law.

3.9 Further Readings

1. **Statistical Thermodynamics**, M.C. Gupta, Wiley Eastern, New Delhi,1990.

2. **Introduction to Statistical Thermodynamics**, R.P.H.Gasser and W.G.Richards, World Scientific, Singapore, 1995.

3. **Physical chemistry**, Peter Atkins, Julio De Paula, 9th edition, 2010

Unit -4: Heat Capacity of solids

Structure

4.0 Introduction

Heat capacity or thermal capacity is a physical property of matter, defined as the amount of heat to be supplied to a given mass of material to produce a unit change in its temperature. The SI unit of heat capacity is joule per Kelvin (J/K). Heat capacity is an extensive property. The corresponding intensive property is the specific heat capacity. Deviding the capacity by the amount of substance in moles yields its molar heat capacity. The volumetric heat capacity measures the heat capacity per volume.

4.1 Objectives

- To understands the heat capacity of the solids and classical observation of heat capacity of solids
- To understand the Einstein theory of heat capacity
- To undertand the Debye theory of heat capacity
- To understand the Non equilibrium thermodynamics and Onsager reciprocal relation.

4.2 Heat capacity

Heat capacity is the quantity of heat required to raise the temperature of the whole of the substance through 1K.

Even at absolute zero the atoms in a solid will be vibrating about their equilibrium positions. When the temperature is increased the amplitude of vibration increases and vibrational energy of the atoms of the solid is increased, it is the rate of change of vibrational energy of the solid with temperature that determine the heat capacity of solids is

NOTE

$$\left(\frac{\partial E_{vib}}{\partial T}\right)_v = C_v$$

4.2.1 Classical observation of heat capacity of solids

An ideal solid is one which consists of space lattice of independent atoms vibrating about their equilibrium positions. They do not interact with each other. Each atom is considered to be a simple harmonic oscillator and can vibrate in three mutually perpendicular direction and can have three vibrational degree of freedom.

According to equipartition principle of energy each vibrational degree of freedom contributes one KT to the total energy of crystal per atom. A solid consisting of 3N atoms will have 3N vibrational degree of freedom and hence will contribute 3NKT or 3RT/gram atom.

$$E_{vib} = 3RT$$

$$C_v = \left(\frac{\partial E_{vib}}{\partial T}\right)_v = \left(\frac{\partial 3RT}{\partial T}\right) = 3R$$

3×1.1987cal/degree/gm.atom

C_v = 5.941 cal/degree/gm.atom

C_v = 3×8.314 cal/degree/gm.atom

C_v = 24.942 cal/degree/gm.atom

According to the classical principle the heat capacity at constant volume must be constant and independent of temperature. Heat capacity measurements are usually made at constant pressure and hence C_v can be converted into Cp using thermodynamic relationship.

$$C_p = C_v + \frac{T.V\alpha V^2}{\beta}$$

Where α_v is the coefficient of thermal expansion and β compressibility factor , V= atomic volume.

4.2.2 Einstein's theory of heat capacity of solids

Classical theories failed to explain its behaviour of variation of atomic heat capacities of solid elements with temperature due to the assumption that solid elements absorb heat continuously. Einstein used Quantum theory to explain all the experimentally observed regarding the variation of heat capacity with temperature.

Assumption of Einstein's theory

1. Heat is absorbed or radiated in the form of discrete packet called photons. Each photon has energy equal to hγ.
2. Each solid consists of atoms arranged in space lattice and are independent.
3. Each atom is considered as a simple harmonic oscillator.
4. The atoms vibrate about their equilibrium position with a uniform frequency which is independent of the presence of neighboring atoms. This frequency is represented as γ and is called Einstein's characteristic frequency.
5. The frequency of vibration of atom is characteristic of the particular solid concerned.
6. Each atom has got 3 independent vibrational degrees of freedom.
7. The average 'E' per degree of freedom is not equal to 'Kt" given by equipartition principle, but is equal to $\frac{hv}{e^{hv/KT}-1}$ as calculated b planck's using quantum theory.

Vibrational energy associated with one atom

$$=\frac{hv}{e^{hv/KT}-1}$$

Vibrational energy associated with 3N atom

$$=\frac{3Nhv}{e^{hv/KT}-1}$$

Heat capacity at constant volume

$$C_V=\left(\frac{\partial E_{vib}}{\partial T}\right)_V$$

NOTE

$$C_v = \frac{\partial}{\partial T}\left(\frac{3Nh\nu E}{e^{h\nu/KT}-1}\right)$$

$$= 3Nh\nu E \frac{\partial}{\partial T}(e^{h\nu E/KT}-1)^{-1}$$

Multiplied and divided by K

$$= 3Nh\nu E \frac{e^{h\nu E/KT}}{(e^{h\nu E/KT}-1)^2} \frac{h\nu E}{KT^2}$$

$$= 3NK\left(\frac{h\nu E}{KT}\right)^2 \cdot \frac{e^{h\nu E/KT}}{(e^{h\nu E/KT}-1)^2}$$

$$= 3R.\frac{e^{h\nu E/KT}}{(e^{h\nu E/KT}-1)^2}\left(\frac{h\nu E}{KT}\right)^2 \rightarrow (1)$$

$$\theta_E = \frac{h\nu E}{K}$$

N_A= Avagadro number

n = number of gram atoms

N = N_A , N_{Ak} = R

Put θ_E = hνE/K, where θ_E is called Einstein's characteristic temperature.

$$C_v = 3R\frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}\left(\frac{\theta_E}{T}\right)^2 \rightarrow (2)$$

Equation (1) and (2) are called Einstein's heat capacity equation.

Factor explained by Einstein's theory

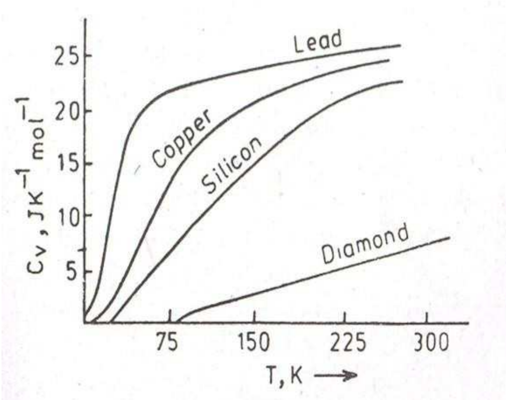
According to Einstein's theory heat capacity equation

1. Cv varies with temperature. It is a function of and it is

related to temperature in an exponential manner.

2. It explains the shape of the curve . since θ_E is related to ν_E as $\theta_E = \frac{h\nu_E}{K}$, Cv is a function of ν_E /T, ν_E is the Einsteins characteristic of the element under consideration. The solid having more or less comparable ν_E values will have the same type of curve. When Cv is plotted as a function of T/θ_E for many elements the following graph is obtained .

NOTE



3. As T→0 Cv attains zero value

Einsteins heat capacity equation is

$$C_v = 3R\frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}\left(\frac{\theta_E}{T}\right)^2$$

As T→0, θ_E /T→∞ , e $^{\theta_E/T}$ >>1.

And hence 'I' in the denominator of Einsteins heat capacity of equation can be neglected and hence the equation becomes

$$C_V = 3R.\frac{e^{\theta_E/T}}{(e^{\theta_E/T})^2}.\left(\frac{\theta_E}{T}\right)^2 = 3R\left(\frac{\theta_E}{T}\right)^2.e^{-\theta_E/T}$$

NOTE

$$\text{As } T \to 0$$

$$e^{-\theta_E/T} \to e^{-\alpha} = 0$$

$$\text{Hence } C_v = 0$$

4. As T→∞ Einsteins equation reduces to Dulong and Petits law is $C_v = 3R$ Einsteins Equation is

$$C_v = 3R \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \left(\frac{\theta_E}{T}\right)^2$$

As T→∞, θ_E/T will tend to zero θ_E/T is expanded as power series of θ_E/T.

$$(e^{\theta_E/T} - 1)^2 = \left(1 + \frac{(\theta_E/T)}{1!} + \frac{(\theta_E/T)^2}{2!} + \frac{(\theta_E/T)^3}{3!} + \;\; - 1\right)^2$$

$$= \left(\frac{\theta_E}{T}\right)^2 \left(1 + \frac{(\theta_E/T)}{2!} + \frac{(\theta_E/T)^2}{3!} + \ldots\ldots\ldots\ldots\ldots\ldots\right)^2$$

As T→∞, θ_E/T will be very small and except to I terms all other terms can be neglected. Hence,

$$(e^{\theta_E/T} - 1)^2 \approx \left(\frac{\theta_E}{T}\right)^2$$

As T→∞, substituting this condition in the Einstein heat capacity equation

$$C_V = 3R \frac{e^{\theta_E/T}}{(\theta_E/T)^2} \times \left(\frac{\theta_E}{T}\right)^2 = 3R.e^0 = 3R$$

As T→∞, $C_v = 3R$. This is Dulong petits law.

Limitations

1. It predicted satisfactorily the value of specific heat of solids at high temperature. But at low temperature the predicted value are found to be lesser than the experimental values.

2. It fails to describe the behaviour of crystals near absolute zero. Failure of this theory is due to the assumption that all the atoms in the crystals are independent and oscillate with uniform frequency. He neglected the mutual forces exerted by the atom upon each other Debye modified Einstein's theory.

4.2.3 Debye theory of heat capacity of solids

Einsteins theory fails to describe adequately the behaviour of crystals near absolute zero. Failure of Einstein's theory is due to the assumption that all the atoms in a solid oscillate with uniform frequency. He neglected the mutual forces between the atoms. Due to Proximity of atoms in a solid there will be interaction and hence the atoms cannot osciallate with uniform frequency. A solid containing N atoms will behave as N coupled oscillators and their frequency will vary from zero to a maximum value (ν_{max}). In order to determine the distribution of frequencies Debye disregarded the structure of the solid and he treated it as a homogeneous continuous elastic medium the vibrations of atoms are considered as equivalent to elastic waves propagated in the elastic medium with different frequencies.

When a continous solid is subjected to elastic vibrations, two kinds of vibrations are produced.

1. Transverse vibration and
2. longitudinal vibrations

According to vibrational theory

Number of modes of longitudinal vibrations

Per unit volume with frequencies in the range ν+dν is= $\frac{4\pi\nu^2 d\nu}{C^l}$ 3

Where --- is the velocity of the longitudinal vibrations.

NOTE

Number of modes of transverse vibrations

Per unit volume with frequencies in the range ν and ν+d ν is =

$$= 2 \times \frac{4\pi\nu^2 d\nu}{C_t^3}$$

Where C_t is the velocity of transverse vibrations (since transverse vibrations have two independent directions of motion $\frac{4\pi\nu^2 d\nu}{C_t^3}$ is multiplied by 2).

Total number of independent vibrations in the frequency range ν to ν+dν $= 4\pi(\frac{1}{C_l^3} + \frac{2}{C_t^3})\nu^2 d\nu$

If V is the volume of one gram mole of the solid . then,

Total number of vibrations $= \int_0^{\nu_{max}} 4\pi V (\frac{1}{Cl^3} + \frac{2}{Ct^3})\nu^2 d\nu$

$$= 4\pi v(\frac{1}{Cl^3} + \frac{2}{Ct^3}).\frac{\gamma_{max}^3}{3}$$

where $\nu_{max} = \nu_D$ is called Debye characteristic frequency.

If there are N atom in volume V the possible vibrational degrees of freedom = 3N

Hence

$$3N = 4\pi v(\frac{1}{Cl^3} + \frac{2}{Ct^3}).\frac{\gamma_{max}^3}{3}$$

$$\frac{9N}{v_m^3} = 4\pi v(\frac{1}{Cl^3} + \frac{2}{Ct^3})$$

The degeneracy associated with a range of frequencies from ν and ν+dν was calculated by Debye using vibration theory. It is found to be proportional to ν^2+dν.

$$dg \propto v^2 dv$$

$$dg = cv^2 dv \text{ where } c = 4\pi v(\frac{1}{Cl^3} + \frac{1}{Ct^3})$$

NOTE

$$dg = 4\pi v\left(\frac{1}{Cl_3} + \frac{2}{Ct_3}\right).\gamma^2\, dv$$

$$dg = \frac{9N}{v_m^3} v^2 dv$$

Total number of vibrational degrees of freedom in a crystal consisting of N atoms will be

$$dg = \frac{9N}{v_m^3} v^2 dv$$

$$dg = \frac{9N}{v_D^3} v^2 dv$$

According to Debye the total energy of a crystal is obtained by adding the energies associated with all the various vibrational frequencies property weighed by their degeneracies.

Average energy of an oscillator is $<E_v> = \frac{hv}{2} + \frac{hv}{e^{hv/KT} - 1}$

Where hv/2 is the zero point energy.

Total vibrational energy of a crystal

$$\int_0^{\gamma_{max}} < Ev >$$

The first integrand on integration gives the total ZPE of the crystal, which is equal to

$$E = \int_0^{v_{max}} \left(\frac{hv}{2} + \frac{hv}{(e\,hv/KT - 1)} \cdot \frac{9Nv^2 dv}{v_{max}^3}\right)$$

$$\left[\int_0^{v_{max}} \frac{hv}{2} \cdot \frac{9Nv^2 dv}{v_{max}^3} = \int_0^{v_{max}} \frac{9Nhv^3 dv}{2v_{max}^3} = \frac{9Nh}{2v_m^3} \frac{v^4}{4}\right]_0^{v_{max}} = \frac{9Nhv_{max}}{8}$$

The energy is excess of zero point enery

$$E = \frac{9Nh}{v_{\max}^3} \int_0^{v_{\max}} \frac{v^3 dv}{e^{hv/KT} - 1}$$

$$\text{put, } x = hv/KT \quad v^4 = \frac{x^4 k^4 T^4}{h^4}$$

$$v = \frac{x.KT}{h} \qquad 4v^3\, dv = \frac{k^4 T^4}{h^4}.4x^3 dx$$

When $v = v_{\max}$ and applying limits from 0 to x, we get

$$E = \frac{9Nh}{v_m^3} \frac{(KT)^4}{h^4} \int_0^{hv_{\max}/kt} \frac{x^3}{e^x - 1} dx$$

Let $v_{o} = v_{\max}$ be the Debye characteristic temperature defined mathematically as $\theta_D = \frac{hv_D}{K} = \frac{hv_{\max}}{K}$

Where θ_D is the Debye characteristic frequency.

$$E = \frac{9RT^4}{\theta_D^3} \int_0^{\theta_D/T} \frac{x^3}{e^{x-1}} dx$$

This is integral can be evaluated in two special cases.

1. At moderate and high temperature above 30K. and
2. At very low temperature below 30K.

Debye theory at moderate and high temperature

$$E = \frac{9RT^4}{\theta_D^3} \int_0^{\theta/T} \frac{x^3}{e^{x-1}} dx$$

For value of T/θ the integral can be evaluated by following series expansion. For large value of T/θ the

NOTE

upper limit of the integration becomes small. First e^x is expanded as a power series and divided it into x^3 by long division.

$$\frac{x^3}{e^{x}-1} = x^2 - \frac{x^3}{2} + \frac{x^4}{12} - \frac{x^6}{760} + \ldots\ldots\ldots\ldots\ldots$$

$$E = \frac{9RT^4}{\theta_D^{\;3}} \int_0^{\theta_D/T} \left(x^2 - \frac{x^3}{2} + \frac{x^4}{12} - \frac{x^6}{760} + \right)dx$$

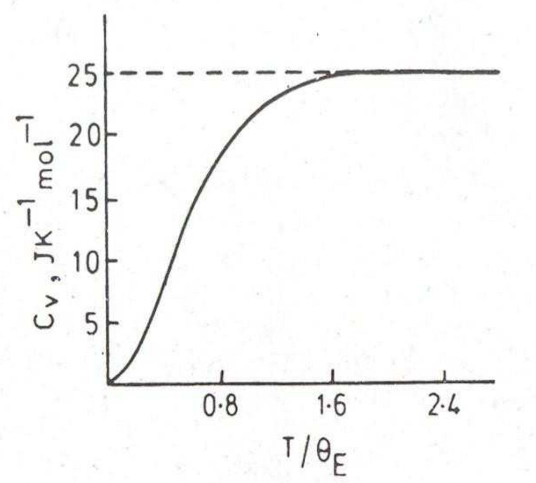
Upon integration

$$E = 3RT\left(1 - \frac{1}{20}(\theta/T)^2 + \frac{1}{560}(\theta/T)^4 - \right)$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3R\left(1 - \frac{1}{20}(\theta/T)^2 + \frac{1}{560}(\theta/T)^4 - \right)$$

As T→∞ the heat capacity approaches 3R as predicted by Einsteins theory

1. Cv is a function of θ_D/T only and a plot of Cv against T/θ_D or log T/θ_D should yield a curve that is the same for all the solids, the curves are called Debye curves.



NOTE

2. From the curve it is evident that heat capacity of an element attains it's classical

value of 3R when T/θ_D is unity.

3. From Debye equation it is possible to calculate the heat capacity of any solid element at all moderate and high temperatures if Debye characteristic temperature is known.

Debye equation at low temperature below 30K

$$E = \frac{9RT^4}{\theta_D^3} \int_0^{\theta_D/T} \frac{x^3 dx}{e^{x-1}}$$

when $T/\theta \rightarrow 0$, $\theta/T \rightarrow \infty$

Hence, $$E = \frac{9RT^4}{\theta_D^3} \int_0^{\infty} \frac{x^3 dx}{e^{x-1}}$$

$$\int_0^{\infty} \frac{x^3 dx}{e^{x-1}} = \frac{\pi^4}{15}$$

$$\therefore E = \frac{9RT^4}{\theta_D^3} \cdot \frac{\pi^4}{15}$$

$Cv = \left(\frac{\partial E}{\partial T}\right)_V$ upon differentiating of energy with respect to temperature

$$Cv = \frac{\partial}{\partial T}\left(\frac{9RT^4}{\theta_D^3 .15} .T^4\right)$$

$$Cv = \frac{9R\pi^4}{\theta_D^3 .15} .T^4$$

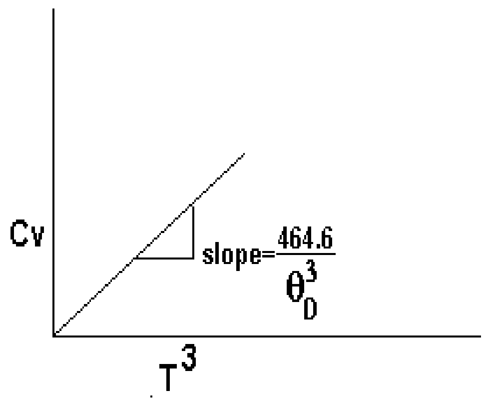
NOTE

$$Cv = \frac{36R\pi^4}{15} \cdot \left(\frac{T}{\theta_D}\right)^3$$

$$Cv = 464.6 . \left(\frac{T}{\theta_D}\right)^3$$

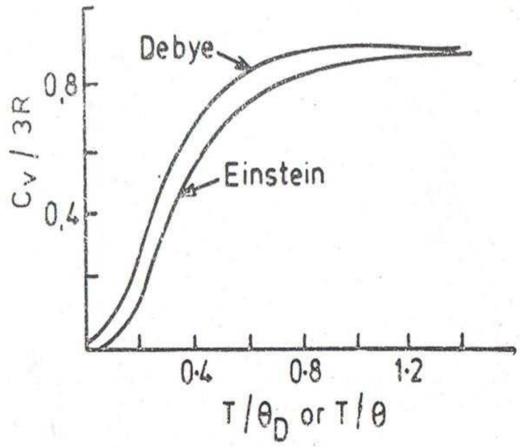
This equation is called Debye third power law.

1. According to this equation the atomic heat capacity of elements is proportional to T^3 or $Cv^{1/3}$.
2. It is used to determine the heat capacity at very low temperature by extrapolation of the curve. This is used to determine the absolute entropies of substances using 3rd law of the thermodynamics.
3. θ_D can be obtained from the slope of the curve obtained by plotting Cv vs. T^3.



4. When θ_D is known, Debye characteristic frequency ν_D or ν_{max} can be calculated using the expression $\theta_D = h\nu_D / K$.
5. The most significant difference between the two theories i.e. Einstein and Debye theories is at low temperature. The debye expression for Cv approaches zero much less rapidly as T→O than does the Einstein's predictions.

NOTE



It is in this respect Debye theory is superior to Einstein theory.

Limitations of Debye theory

1. θ_D should be independent of the source of measurement but it is not.
2. θ_D Vs T should be a horizontal straight line since θ_D is a constant and independent of temperature. But there are deviations in the case of Ag and Na I.
3. In the case of metals there is electronic contribution to the heat capacity due to free electrons, which has not been taken into account
   $Cv = R(T/T_f)$ **,** T_f –fermi temperature.
4. Debye theory considers the solid to be a homogeneous continous elastic medium without any definite structure. It may not be exactly correct.

4.3 Non equilibrium thermodynamics

The branch of science dealing with the study of thermodynamic properties of the system which are not in equilibrium and involves transport process which are irreversible is termed as irreversible or non equilibrium thermodynamics.

Onsager reciprocal relation

4.3.1 Postulates of local equilibrium Onsager

formulation

Phenomenological laws, onsager reciprocal relations.

Onsager theory is based on the principle of microscopic reversibility which states that under equilibrium conditions any molecular process and the reverse of this process will be taking place on the average at the same rate. According to onsager, the rates or velocities of the various types of processes like diffusion, flow o heat etc are linearly related to 'thermodynamic forces'. These are driving forces responsible for the transport processes.

NOTE

For example, temperature gradient is responsible for flow of heat, and a gradient of chemical potential is the driving force for diffusion. If J is taken as the rate of flow or flux and x as the force, the flux- force relationship is of the form

J = LX

Linear laws of this kind are called the phenomenological relations. At thermodynamic equilibrium for all processes, the forces X_k and hence the flows, J_K in the system are zero.

Consider a system in which a temperature gradient, X_1 and also a concentration gradient X_2 exist. There will be a flow of heat and flow of matter. Let J_1 and J_2 represent the rate of flow of heat and the rate of flow of matter respectively. If these takes place separately. $J_1 \alpha X_1$ and $J_2 \alpha X_2$. According to onsager, if both he processes occur simultaneously, near equilibrium the flows and fluxes are related by the phenomenologicals equations.

$$J_1 = L_{11}X_1 + L_{12}X_2 \qquad \textbf{(1)}$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \qquad \textbf{(2)}$$

In these equations,

'L_{11}' is the thermal conductivity coefficient which relates J_1 and X_1.

NOTE

'L_{22}' is the diffusion coefficient which relates J_2 and X_2

'L_{12}' and L_{21} the cross coefficients describes the coupling of the two irreversible processes 1 and 2. These are called drag co-efficient.

'L_{12}' represents the heat flow arising from a concentration gradient.

'L_{2i} gives the flow of matter in response to a temperature gradient.

Eqn 1 and 2 can be written as

$$J_i = L_{ii} X_i + L_{ik} X_k$$

$$J_k = L_{ki} X_i + L_{kk} X_k$$

The coefficients L_{iK}, L_{Ki} L_{ii} L_{kk} are called phenomenological coefficients L_{ii} L_{kk} are speciall referred to as the direct co-efficients. while L_{ik} and L_{ki} are referred to as cross coefficients.

The rate of entropy production is given by equation

$\sum J_k X_k > 0$

Substituting for the J_k from equations

$$d_i s / dt = L_{11} X_1^2 + (L_{12} + L_{21}) X_1 X_2 + L_{22} X_2^2 > 0$$

This quadratic equation will be positive if both X_1 and X_2 have the same sign and becomes zero when $X_1 = X_2 = 0$.

The phenomenological coefficients must satisfy the following conditions

$$L_{11} > 0,\ L_{22} > 0$$

$$(L_{12} + L_{21})^2 < 4 L_{11} L_{22} \quad (\because b^2 = 4ac)$$

This can be shown as

$$L_{11} X_1^2 + (L_{12} + L_{21}) X_1 X_2 + L_{22} X_2^2 > 0$$

$$L_{11} \{X_1^2 + (\frac{L_{12} + L_{21}}{L_{11}}) X_1 X_2 + \frac{L_{22}}{L_{11}} X_2^2\} > 0$$

$$L_{11}\{X_1^2 + 2aX_1X_2 + a^2X_2^2 + \frac{L_{22}}{L_{11}}X_2^2 - a^2X_2^2\} > 0$$

$$\textbf{where, } 2a = \frac{L_{12} + L_{21}}{L_{11}}$$

$$L_{11}\{(X_1 + aX_2)^2 + \frac{L_{22}}{L_{11}}X_2^2 - \left(\frac{L_{12} + L_{21}}{2L_{11}}\right)^2 X_2^2\} > 0$$

$$L_{11}\{(X_1 + aX_2)^2 + \left[\frac{4L_{11}L_{22} - (L_{12} + L_{21})^2}{4L_{11}^2}\right]X_2^2\} > 0 \rightarrow (3)$$

$(X_1 + aX_2)^2$ is always positive. From equation (3), it is seen that

$\frac{4L_{11}L_{22} - (L_{12} + L_{21})^2}{4L_{11}^2}$ must also be positive**.**

Otherwise the term within { } will have a sign which depends on the magnitude of X_2 L_{11}^2 is positive.

So $(L_{12} + L_{21})^2 < 4L_{11}L_{22}$.

Since the term within the brackets { } is positive $L_{11}>0$.

Since $(L_{12} + L_{21})^2 > 0$ **,** $4L_{11}L_{22} > 0$, $L_{22} > 0$

Onsager showed that if fluxes and forces are properly chosen, the cross coefficients become equal

i.e $L_{12} = L_{21}$ or $L_{ik} = L_{ki} \rightarrow (4)$

This equation (4) is called onsager's reciprocal relation.

4.4 Check Your Progress

1. Define Heat capacity.
2. What are all the limitations of debye theory of heat capacity of solids.

NOTE

3. Define Non equilibrium thermodynamics.

4.5 Answers to check your progress questions

1. Heat capacity is the quantity of heat required to raise the temperature of the whole of the substance through 1K. Even at absolute zero the atoms in a solid will be vibrating about their equilibrium positions. When the temperature is increased the amplitude of vibration increases and vibrational energy of the atoms of the solid is increased, it is the rate of change of vibrational energy of the solid with temperature that determine the heat capacity of solids is

$$\left(\frac{\partial E_{vib}}{\partial T}\right)_v = C_v$$

2. Limitations of Debye theory

- θ_D should be independent of the source of measurement but it is not.
- θ_D Vs T should be a horizontal straight line since θ_D is a constant and independent of temperature. But there are deviations in the case of Ag and Na I.

- In the case of metals there is electronic contribution to the heat capacity due to free electrons, which has not been taken into account
$Cv = R(T/T_f)$, T_f –fermi temperature.

- Debye theory considers the solid to be a homogeneous continous elastic medium without any definite structure. It may not be exactly correct.

3. Non equilibrium thermodynamics

The branch of science dealing with the study of thermodynamic properties of the system which are not in equilibrium and involves transport process which are irreversible is termed as irreversible or non equilibrium thermodynamics.

4.6 Summary

Heat capacity is the quantity of heat required to raise the temperature of the whole of the substance through 1K.

Einstein theory of heat capacity of solids: Classical theories failed to explain its behaviour of variation of atomic heat capacities of solid elements with temperature due to the assumption that solid elements absorb heat continuously. Einstein used Quantum theory to explain all the experimentally observed regarding the variation of heat capacity with temperature.

Debye theory of heat capacity of solids: Einsteins theory fails to describe adequately the behaviour of crystals near absolute zero.

In order to determine the distribution of frequencies Debye disregarded the structure of the solid and he treated it as a homogeneous continuous elastic medium the vibrations of atoms are considered as equivalent to elastic waves propagated in the elastic medium with different frequencies.

Non equilibrium thermodynamics: The branch of science dealing with the study of thermodynamic properties of the system which are not in equilibrium and involves transport process which are irreversible is termed as irreversible or non equilibrium thermodynamics.

Onsager reciprocal relation: In thermodynamics, the Onsager reciprocal relations express the equality of certain ratios between flows and forces in thermodynamic systems out of equilibrium, but where a nation of local equilibrium exist.

Reciprocal relations occur between different pairs of forces and flows in a variety of physical systems.

NOTE

4.7 Keywords

Heat capacity

a) The constant-volume heat capacity can be calculated from the molecular partition function.

b) The total heat capacity of a molecular substance is the sum of the contributions of each mode.

Einstein used Quantum theory to explain all the experimentally observed regarding the variation of heat capacity with temperature.

In order to determine the distribution of frequencies **Debye** disregarded the structure of the solid and he treated it as a homogeneous continuous elastic medium the vibrations of atoms are considered as equivalent to elastic waves propagated in the elastic medium with different frequencies.

Non equilibrium thermodynamics: Thermodynamic properties of the system which are not in equilibrium and involves transport process which are irreversible is termed as irreversible or non equilibrium thermodynamics.

Onsager reciprocal relation: In thermodynamics, It’s explains the the equality of certain ratios between flows and forces in thermodynamic systems out of equilibrium, but where a nation of local equilibrium exist.

4.8 Self-assessment questions and exercises

1. Define Heat Capacity and explain the Debye theory of heat capacity of solids.
2. Explain the Einstein theory of heat capacity of solids.
3. Derive Onsager reciprocal relation.

4.9 Further Readings

1. **Statistical Thermodynamics**, M.C. Gupta, Wiley Eastern, New Delhi,1990.

2. **Introduction to Statistical Thermodynamics**, R.P.H.Gasser and W.G.Richards, World Scientific, Singapore, 1995.

NOTE

NOTE

BLOCK – 2: QUANTUM CHEMISTRY

Unit-5: Quantum Chemistry

Structure

5.0 Introduction

There are several areas of chemistry that require a knowledge of quantum
Mechanics for their explanation and understanding.Therefore quantum
Mechanics at an elementary level is covered in several physics and chemistry.We will introduce some of the procedures and terminology of quantum mechanics and some of their applications.Here complete coverage of quantum mechanics and its applications given below.

5.1 Objectives

After going through this unit, you will be able to:

- Understand about the one dimensional harmonic Oscillator.
- Understand the concept of rigid rotator.

5.2 One Dimensional Harmonic Oscillator

Vibration of a diatomic molecule can be described by a harmonic oscillator. Consider the simple harmonic motion of a single particle of mass m attached to a point and oscillating to and fro about its equilibrium position.

Restoring force (f) acting on the particle is proportional to the displacement x from the equilibrium position.

$$f \propto x$$
$$f = -Kx$$

This expression is called Hooke’s law. A force of this type is called “harmonic” and the system obeying Hooke’s law is called simple harmonic oscillator.

Potential energy V of such a particle is equal to the integral of this force over the distance it acts

$$V = -\int_0^x f\,.dx = -\int_0^x (-Kx).dx$$

$$= -\left(-\frac{Kx^2}{2}\right)_0^x$$

Potential energy V= $+\dfrac{Kx^2}{2}$

Total energy of Harmonic oscillator $\hat{H} = \hat{T} + \hat{V}$

$$\hat{H} = \left(-\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}Kx^2\right)$$

Schrodinger equation representing the system of one dimensional simple harmonic oscillator is

$$\left(-\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V\right)\psi(x) = E\psi(x)$$

upon rearranging

$$\frac{\partial^2}{\partial x^2}\psi(x) + \frac{8\pi^2 m}{h^2}\left(E - \frac{1}{2}Kx^2\right)\psi(x) = 0 \rightarrow (1)$$

Let $\alpha = \dfrac{8\pi^2 m}{h^2}E$; $\beta^2 = \dfrac{8\pi^2 m\,K}{h^2\;2}$; $\beta = \sqrt{\dfrac{8\pi^2 mK}{2h^2}}$

$$\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2 m}{h^2}E\psi(x) - \frac{8\pi^2 m}{h^2}\cdot\frac{Kx^2}{2}\psi(x) = 0$$

$$\frac{d^2\psi(x)}{dx^2} + \left(\alpha - \beta^2 x^2\right)\psi(x) = 0 \rightarrow (2)$$

Changing the variable to

$$\xi = \sqrt{\beta} \times x$$

$$x = \frac{\xi}{\sqrt{\beta}}$$

$$x^2 = \frac{\xi^2}{\beta}$$

Equation (2) becomes

$$\beta\frac{d^2\psi(\xi)}{d\xi^2\sqrt{\beta}} + \left(\alpha - \frac{\beta^2\xi^2}{\beta}\right)\frac{\psi(\xi)}{\sqrt{\beta}} = 0$$

Dividing through out by β and multiply by √β

$$\frac{d^2\psi(\xi)}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi(\xi) = 0 \rightarrow (3)$$

Eigen function:

$\psi(\xi)$ is the solution of this equation. But it is not easy to find the solution of this second order differential equation. Hence this equation is compared with the second order differential mathematical equation.

$$\frac{d^2u(x')}{dx'^2} + \left((2n+1) - x'^2\right)u(x') = 0 \rightarrow (4)$$

It is the mathematical equation. The solution of this equation is u(x`) and contains a polynomial in x`.

$$u(x') = (-1)^n e^{\frac{x'^2}{2}} \cdot \frac{dn}{dx'^n} e^{-x'^2}$$

$$= (-1)^n e^{\frac{x'^2}{2}} . e^{-x'^2} \frac{dn}{dx'^n} e^{-x'^2}$$

NOTE

$$= e^{-\frac{x'^2}{2}}.H_n(x')$$

where $H_n(x')$ is called Hermite polynomial of degree n and has real roots.

Comparing equation (3) with (4), unnormalised solution of the equation representing simple harmonic oscillator system in its n^{th} quantum state of vibration can be written as

$$\psi(\xi) = e^{\frac{-\xi^2}{2}}.H_n(\xi)$$

where $H_n(\xi)$ is called Hermite polynomial of degree n and has real roots.

$$\xi = \sqrt{\beta}.x$$

$$\psi(\sqrt{\beta}x) = e^{-\frac{\beta x^2}{2}}.H_n(\sqrt{\beta}x)$$

Normalization of the wave function for the oscillator is carried out as follows

$$\langle\psi_n(\xi)/\psi_n(\xi)\rangle = N = \frac{2^n n!\sqrt{\pi}}{\sqrt{\beta}}$$

$$[-\infty,+\infty]$$

Hence normalized solution for the harmonic oscillator is

$$\psi_n(\xi) = \left(\frac{\sqrt{\beta}}{2^n n!\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{\xi^2}{2}}.H_n(\xi) \text{ and}$$

$$\psi_n(x) = \left(\frac{\sqrt{\beta}}{2^n n!\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{\beta x^2}{2}}.H_n(\sqrt{\beta}x)$$

$$H_n(x) = (-1)^n.e^{x^2}.\frac{\partial n}{\partial x^n} e^{-x^2}$$

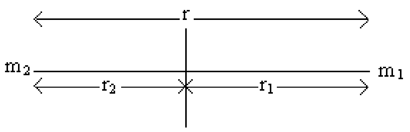
$$H_n(\sqrt{\beta}x) = H_n(\sqrt{x})$$

5.3 Rigid Rotor

NOTE

Rigid Rotor consists of two spherical particles attached together and the particles are separated by a finite fixed distance.

Consider a rigid rotor model consisting of two masses m_1 and m_2 at a distances r_1 and r_2 respectively from the centre of gravity of the system. Let 'ν' be the distance between the two masses and this distance remains unchanged during rotation and hence it is a rigid rotor model.



Moment of inertia of a rigid rotor:

Moment of inertia of the molecule about an axis perpendicular to the plane of the molecule is

$$I = \sum m_i r_i^2$$

To get 'I' in terms of 'r'. Consider the following quantities.

$$r = r_1 + r_2$$

$$r_2 = r - r_1$$

$$m_1 r_1 = m_2 r_2$$

$$I = m_2 r_2 r_1 + m_1 r_1 r_2$$

$$= r_1 r_2 (m_1 + m_2)$$

$$m_1 r_1 = m_2 r_2 = m_2 (r - r_1)$$

$$r_1 = \frac{m_2}{m_1 + m_2} r \quad ; \quad r_2 = \frac{m_1}{m_1 + m_2} r$$

$$I = \frac{m_1 m_2^2}{(m_1 + m_2)^2} r^2 + \frac{m_1^2 m_2}{(m_1 + m_2)^2} r^2$$

$$I = \frac{m_1 m_2^2 + m_1^2 m_2}{(m_1 + m_2)^2} r^2$$

$$I = \frac{m_1 m_2 (m_1 + m_2)}{(m_1 + m_2)^2} r^2 = \frac{m_1 m_2}{(m_1 + m_2)} r^2 = \mu r^2$$

Schrodinger wave equation for rigid rotor

Total energy H = Kinetic energy + Potential energy

H = T +V Potential energy 'V' is taken as zero

Hence H = T + 0

And $\hat{H} = \hat{T}$

Let v_1 and v_2 be the velocities of the two particles of mass m_1 and m_2 respectively then

Kinetic energy of the rigid rotor

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$$

Linear velocity 'v' is related to angular velocity 'ω' as ω= v/r , where 'r' is the radius.

$v_1^2 = \omega^2 r_1^2$; $v_2^2 = \omega^2 r_2^2$

$$\therefore T = \frac{1}{2} m_1 \omega^2 r_1^2 + \frac{1}{2} m_2 \omega^2 r_2^2$$

NOTE

$$= \frac{1}{2}\omega^2\left(m_1 r_1^2 + m_2 r_2^2\right)$$

$$T = \frac{1}{2}\omega^2 I$$

$$T = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I}$$

where L is total angular momentum

$$\hat{H} = \hat{T} = \frac{\hat{L}^2}{2I}$$ for a rigid rotor

Schrodinger wave equation for a rigid rotor is

$$\hat{H}\psi(\theta,\phi) = E\psi(\theta,\phi)$$

$$\frac{\hat{L}^2}{2I}\psi(\theta,\phi) = E\psi(\theta,\phi)$$

In spherical polar co-ordinate system

$$\hat{L}^2 = \frac{-h^2}{4\pi^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Hence shcrodinger wave equation becomes,

$$\frac{-h^2}{4\pi^2}\cdot\frac{1}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(\theta,\phi) = E\psi(\theta,\phi)$$

upon rearranging we get

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\psi(\theta,\phi)\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\psi(\theta,\phi)\right] + \frac{8\pi^2 I}{h^2}E\psi(\theta,\phi) = 0$$

This is Schrodinger wave equation representing rigid rotor.

This equation contains two angular variables, θ and Φ and is 2nd order partial differential equation. This equation is separated into two equations, which are total differential equations by using the separation of variable procedure and solved.

Separation of variables:

Total wave function is written as the product of two wave functions, which are dependent separately on only one variable and independent of the other and inserted in the equation

$$\psi(\theta,\phi) = \theta_{(\theta)}\phi_{(\phi)}$$

$$\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\theta_{(\theta)}\phi_{(\phi)}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\theta_{(\theta)}\phi_{(\phi)}\right)+\frac{8\pi^2 I}{h^2}E\theta_{(\theta)}\phi_{(\phi)}=0$$

$$\frac{\phi_{(\phi)}}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\theta_{(\theta)}\right)+\frac{\theta_{(\theta)}}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\phi_{(\phi)}+\frac{8\pi^2 I}{h^2}E\theta_{(\theta)}\phi_{(\phi)}=0$$

Multiply by $\frac{\sin^2\theta}{\theta_{(\theta)}\phi_{(\phi)}}$

$$\frac{\sin\theta}{\theta_{(\theta)}}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\theta_{(\theta)}\right)+\frac{1}{\phi_{(\phi)}}\frac{\partial^2}{\partial\phi^2}\phi_{(\phi)}+\frac{8\pi^2 I}{h^2}E\sin^2\theta=0$$

$$\frac{\sin\theta}{\theta_{(\theta)}}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\theta_{(\theta)}\right)+\frac{8\pi^2 I}{h^2}E\sin^2\theta=-\frac{1}{\phi_{(\phi)}}\frac{\partial^2}{\partial\phi^2}\phi_{(\phi)}$$

Left hand side of this equation contains the function of θ and right hand side contains the terms, which depends only on the variable Φ. Both sides are equated to a common constant m^2.

$$\frac{\sin\theta}{\theta_{(\theta)}}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\theta_{(\theta)}}{\partial\theta}\right)+\frac{8\pi^2 I}{h^2}E\sin^2\theta = m^2 \rightarrow (1)$$

NOTE

This is called θ equation.

$$-\frac{1}{\phi_{(\phi)}}\frac{\partial^2}{\partial\phi^2}\phi_{(\phi)} = m^2 \rightarrow (2)$$

This equation is called Φ equation.

Solution of Φ equation:

Upon rearranging equation (2)

$$\frac{\partial^2}{\partial\phi^2}\phi_{(\phi)} = m^2\phi_{(\phi)}$$

$$\frac{\partial^2}{\partial\phi^2}\phi_{(\phi)} + m^2\phi_{(\phi)} = 0$$

This equation is called Φ equation.

$\phi_{(\phi)}$ is the solution of this equation.

$$\phi_{(\phi)} = Ce^{\pm im\phi}$$

This is an acceptable solution provided 'm' is an integer

$\phi_{(\phi)} = \phi(\phi + 2\pi)$ Since ϕ is an angle.

$$e^{\pm im\phi} = e^{\pm im(\phi+2\pi)}$$

$$e^{\pm im\phi} = e^{\pm im(\phi)} - e^{\pm im(2\pi)}$$

$$e^{\pm im2\pi} = 1$$

Note:

$$\left(e^{i\theta} = \cos\theta + i\sin\theta\right)$$

$$\cos(2m\pi) + i\sin(2m\pi) = 1$$

This is true only if 'm' can take up 0, ±1, ±2, ±3 etc.

This function $\phi_{(\phi)}$ should be normalized.

$$\langle \phi_{(\phi)} / \phi_{(\phi)} \rangle = 1$$

[0, 2π]

$$\int_0^{2\pi} \phi^*{}_{(\phi)} . \phi_{(\phi)} d\phi = 1 \qquad \left(\phi_{(\phi)} = Ce^{\pm im\phi}\right)$$

$$\int_0^{2\pi} Ce^{\pm im\phi} . Ce^{\pm im\phi} d\phi = 1$$

$$C^2 \int_0^{2\pi} d\phi = 1$$

$$C^2 [\phi]_0^{2\pi} = 0$$

$$C^2 (2\pi - 0) = 1$$

$$C^2 = \frac{1}{2\pi}$$

$$C = \sqrt{\frac{1}{2\pi}}$$

Normalised solution of ϕ equation is $\phi_{(\phi)} = \frac{1}{\sqrt{2\pi}} e^{\pm im\phi}$ where m = 0,1,2,3……….

Solution of θ equation:

The rearranged θ equation is that is equation (1) is multiplied by $\theta_{(\theta)}$ and divided by $\sin^2\theta$.

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\theta_{(\theta)} + \left(\beta - \frac{m^2}{\sin^2\theta}\right)\theta_{(\theta)} = 0$$

NOTE

θ equation is compared with Legendre equation in mathematics. Associated Legendre function is the solution of the mathematical equation. The normalized solution of a equation is

$$\theta_{(\theta)} = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} P_l^m(\cos\theta)$$

$P_l^m(\cos\theta)$ is a polynomial in cos θ of degree l and order $|m|$.

Hence normalised solution of the schrodiner wave equation representing rigid rotor is

$$\psi(\theta,\phi)_{l\pm m} = \theta_{(\theta)\, l\pm m} \cdot \phi_{(\phi)\, l\pm m}$$

$$= \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} P_l^m(\cos\theta) \frac{1}{\sqrt{2\pi}} e^{\pm im\phi}$$

where ‘l’ is a positive quantity. Two quantum conditions are

l = 0, 1, 2, 3…………

m = 0, ±1, ±2, ±3…......... ±l

This solution is called spherical harmonics and is represented as

$$\gamma(\theta,\phi)_{l+m} = \theta_{(\theta)} . \phi_{(\phi)}$$

A few spherical harmonics are

l	m	$\gamma(\theta,\phi)_{l\pm m}$	$= \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}} P_l^m(\cos\theta) \frac{1}{\sqrt{2\pi}} e^{\pm im\phi}$
0	0	$\gamma(\theta,\phi)_{0,0}$	$= \frac{\sqrt{2}}{2} \cdot \frac{1}{\sqrt{2\pi}} = \frac{1}{2\sqrt{\pi}}$

1 0 $\gamma(\theta,\phi)_{1,0} = \frac{\sqrt{3}}{2\sqrt{\pi}}\cos\theta$

Energy of Rigid Rotor:

Comparing the two equation

$$(1-x^2)\frac{\partial^2 u(x)}{\partial x^2} - 2x\frac{\partial u(x)}{\partial x} + \left(l(l+1) - \frac{m^2}{1-x^2}\right)u(x) = 0$$

when $x = \cos\theta$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\theta_{(\vartheta)} + \left(\beta - \frac{m^2}{\sin^2\theta}\right)\theta_{(\vartheta)} = 0$$

we get $\beta = l(l+1)$

$$= \frac{8\pi^2 IE}{h^2} = (l(l+1))$$

$$E_{rot} = \frac{l(l+1)h^2}{8\pi^2 I} \text{ where l = 0,1,2}$$

1. Energy of the rigid rotor depends on the values of l and independent of ‘m’.
2. Energy of rigid rotor is quantized.
3. Energy increases with increases in ‘l’ value.

5.4 Check Your Progress

1. What is meant by Hooks law?
2. What is wave function?

5.5 Answers to Check Your Progress Questions

NOTE

1. Hooke's law is named for Robert Hooke,According to the Hooke's law ,for a particle executing simple harmonic motion in one direction, the restoring force F is directly proportional to the displacement x from the equilibrium position

$$F \ \alpha - x$$

$$F = -k\,x$$

The negative sign indicates that the displacement x and the restoring force F are in opposite directions.K is proportionality constant called the force constant.

2. The eigenfunctions of a quantum mechanical operator depend on the coordinates upon which the operator acts; these functions are called wavefunctions.

5.6 Summary

- According to classical mechanics, the state of a system is specified by giving the position and velocity of every particle in the system. Consider a single particle withoutany internal structure so that it cannot rotate or vibrate.
- If it can move in three dimensionswe can specify its position by the three Cartesian coordinates *x*, *y*, and *z*.
- These three coordinates are equivalent to a *position vector* that reaches from the origin of coordinates to the location of the
- particle.
- The Cartesian coordinates *x*, *y*, and *z* are called the *Cartesian components* of the position vector **r**.A vector can also be denoted by listing its three Cartesian components inside parentheses, as in (*x*, *y*, *z*)
- In order to show how Newton's laws determine the behavior of a particle, we apply them to a harmonic oscillator, which is a model system designed to represent a mass attached to a stationary object by a spring, A *model system* is designed to imitate a real system, but is defined to have simpler properties so that it canbe analyzed more easily.
- Let the horizontal coordinate *x* of the mass equal zero at its equilibrium position and assign it to be positive if the spring is stretched and negative if the spring is compressed.

5.7 Keywords

- **Harmonic oscillator:** A System which,when displaced from its equilibrium position,experiences a restoring force proportional to the displacement according to Hooks Law.

- **Rigid Rotator:** The rigid rotator is a simple model of a rotating diatomic molecule.

5.8 Self-assessment questions and exercises

1. The frequency of vibration of a 1H35Cl molecule is
8.966 × 1013 s−1.
a. What would the frequency be if the chlorine atom were infinitely massive?
b. What would the frequency be if the hydrogen atom were infinitely massive?

2. What do you mean rigid rotator? Write a note on rigid rotator in a plane.
3. Apply Schrödinger wave equation to a system of rigid rotor and solve the equation

5.9.Furthur readings

1. **Quantum Chemistry**, I.N. Levine, Allyn and Bacon, Boston, 1983.
2. **Quantum Chemistry**, R.K.Prasad, Wiley stern, New Delhi,1992.

NOTE

Unit- 6 Quantum Mechanical Treatment

6.0 Introduction.

In this unit we can elaborately understand Quantum mechanical treatment for radial and angular wave function and hydrogen atom like atoms.

6.1 Objectives

After going through this unit, you will be able to:

- Understand the concept of Quantum mechanical treatment.
- Understand pauli's exclusion principle and slater determinant.
- Learn about the Approximation methods.

6.2 Quantum mechanical treatment

Hydrogen atom is made up of a proton and an electron revolving the nucleus.

The potential energy of the electron is due to the electrical force of attraction between the electron and the nucleus.

$$\therefore V = -\frac{Ze^2}{r}$$

Therefore Schrodinger equation for the hydrogen like atom can be written as

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0$$

This can be solved by transforming the Cartesian co-ordinates x, y, z into spherical polar co-ordinates r, θ, Φ.

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)\psi = 0 \rightarrow (1)$$

Separation of variables:

$$\psi = R(r).\theta(\theta).\phi(\phi) \rightarrow (2)$$

Substituting (2) in equation (1), we get

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2.\theta(\theta)\phi(\phi)\frac{\partial}{\partial r}R(r)\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta.R(r).\phi(\phi)\frac{\partial}{\partial\theta}\theta(\theta)\right) + \frac{R(r).\theta(\theta)}{r^2\sin^2\theta}.\frac{\partial^2}{\partial\phi^2}\phi(\phi)$$
$$+\frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)R(r).\theta(\theta)\phi(\phi) = 0$$

Multiply by r^2,

$$\theta(\theta)\phi(\phi).\frac{\partial}{\partial r}\left(r^2.\frac{\partial}{\partial r}R(r)\right) + \frac{R(r).\phi(\phi)}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\theta(\theta)\right) + \frac{R(r).\theta(\theta)}{\sin^2\theta}.\frac{\partial^2}{\partial\phi^2}\phi(\phi)$$
$$+\frac{8\pi^2 m r^2}{h^2}\left(E + \frac{Ze^2}{r}\right)R(r).\theta(\theta)\phi(\phi) = 0$$

Divide by $R(r).\theta(\theta).\phi(\phi)$

Unit -6 Quantum Mechanical Treatment

NOTE

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial}{\partial r}R(r)\right)+\frac{1}{\theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\theta(\theta)\right)+\frac{1}{\phi(\phi)\sin^2\theta}\cdot\frac{\partial^2}{\partial\phi^2}\phi(\phi)+\frac{8\pi^2mr^2}{h^2}\left(E+\frac{Ze^2}{r}\right)=0$$

Multiply by $\sin^2\theta$,

$$\frac{\sin^2\theta}{R(r)}\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial}{\partial r}R(r)\right)+\frac{\sin\theta}{\theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\theta(\theta)\right)+\frac{1}{\phi(\phi)}\cdot\frac{\partial^2}{\partial\phi^2}\phi(\phi)+\frac{8\pi^2mr^2\sin^2\theta}{h^2}\left(E+\frac{Ze^2}{r}\right)=0$$

$$\frac{\sin^2\theta}{R(r)}\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial}{\partial r}R(r)\right)+\frac{\sin\theta}{\theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\theta(\theta)\right)+\frac{8\pi^2mr^2\sin^2\theta}{h^2}\left(E+\frac{Ze^2}{r}\right)=-\frac{1}{\phi(\phi)}\cdot\frac{\partial^2\phi(\phi)}{\partial\phi^2}$$

Left hand side of the equation contains the variables r and θ and right hand side contains the variables Φ. Each sides of the equation is equated to a common constant say m^2 such that

$$-\frac{1}{\phi(\phi)}\cdot\frac{\partial^2}{\partial\phi^2}\phi(\phi)=m^2$$

$$\frac{\partial^2}{\partial\phi^2}\phi(\phi)+m^2\phi(\phi)=0\rightarrow(3)$$

The equation (3) is called Φ equation.

$$\frac{\sin^2\theta}{R(r)}\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial}{\partial r}R(r)\right)+\frac{\sin\theta}{\theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\theta(\theta)\right)+\frac{8\pi^2mr^2\sin^2\theta}{h^2}\left(E+\frac{Ze^2}{r}\right)=m^2\rightarrow(4)$$

Divide the equation by $\sin^2\theta$ and upon rearranging

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial}{\partial r}R(r)\right)+\frac{1}{\theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\theta(\theta)\right)+\frac{8\pi^2mr^2}{h^2}\left(E+\frac{Ze^2}{r}\right)=\frac{m^2}{\sin^2\theta}$$

NOTE

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial}{\partial r}R(r)\right)+\frac{8\pi^2 mr^2}{h^2}\left(E+\frac{Ze^2}{r}\right)=\frac{m^2}{\sin^2\theta}-\frac{1}{\theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\theta(\theta)\right)$$

Left hand side as well as right hand side of the equation contains only one variable and hence both must be equated to a common constant β.

$$\frac{m^2}{\sin^2\theta}-\frac{1}{\theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\theta(\theta)=\beta$$

$$-\frac{1}{\theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\theta(\theta)=\beta-\frac{m^2}{\sin^2\theta}$$

Multiplying by $\theta(\theta)$ and rearranging

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\theta(\theta)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\theta(\theta)=0\rightarrow(5)$$

This equation is called θ equation

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial}{\partial r}R(r)\right)+\frac{8\pi^2 mr^2}{h^2}\left(E+\frac{Ze^2}{r}\right)=\beta$$

Multiplying by $R(r)/r^2$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\cdot\frac{\partial}{\partial r}R(r)\right)-\frac{\beta}{r^2}R(r)+\frac{8\pi^2 m}{h^2}\left(E+\frac{Ze^2}{r}\right)R(r)=0\rightarrow(6)$$

This is called radial equation or r equation.

Solution of Φ equation:

Φ equation is

$$\frac{\partial^2}{\partial\phi^2}\phi(\phi)+m^2\phi(\phi)=0$$

The solution of Φ equation is

$$\phi(\phi)=Ce^{\pm im\phi}$$

$\pm m$

NOTE

$$\langle \phi(\phi) / \phi(\phi) \rangle = 1$$
$[0, 2\pi]$

$$\left\langle Ce^{\pm im\phi} / Ce^{\pm im\phi} \right\rangle = \int_0^{2\pi} Ce^{\pm im\phi} . Ce^{\pm im\phi} = 1$$
$[0, 2\pi]$

$$= C^2 \int_0^{2\pi} d\phi = C^2 [\phi]_0^{2\pi} = 1$$

$$C^2 \, 2\pi = 1$$
$$C^2 = \frac{1}{2\pi}$$
$$C = \frac{1}{\sqrt{2\pi}}$$

Normalised solution of Φ equation is

$$\phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm im\phi}$$
$\pm m$

Solution of θ equation:

The θ equation is

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} \theta(\theta) + \left(\beta - \frac{m^2}{\sin^2\theta} \right) \theta(\theta) = 0$$

Associated Legendre function of degree l and order m in the variable cos θ represented as $P_l^m \cos\theta$ is the solution of θ equation.

Normalised solution of θ equation

$$\theta(\theta) = \sqrt{\frac{(2l+m)(l-m)!}{2(l-m)!}} P_l^m \cos\theta$$
$l \pm m$

The product of solutions of θ and Φ equation is spherical harmonics that is

$Y_{l\pm m}(\theta,\phi) = \theta(\theta).\phi(\phi)$

$l \pm m \quad l \pm m$

Solution of radial equation:

Radial equation is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \cdot \frac{\partial}{\partial r}R(r)\right) - \frac{\beta}{r^2}R(r) + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)R(r) = 0$$

The solution of this equation is $R(r)$.

$$R(r) = \sqrt{\left(\frac{2z}{na_0}\right)^3 \frac{4(n-l-1)!}{2n(n+l)^3}}\, e^{-\frac{p}{2}} p^l L_{n+l}^{2l+1}(p)$$

where $p = \frac{2zr}{na_0}$, $a_0 = \frac{h^2}{4\pi^2 e^2 \mu}$, and $L_{n+l}^{2l+1}(p)$ is the associated Laguerre polynomial.

Hence the total solution of the wave equation is

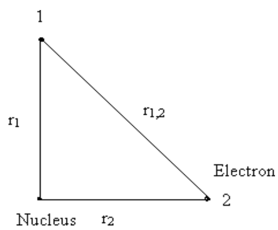
$$\psi(r,\theta,\phi) = R(r),\theta(\theta),\phi(\phi)$$

n, l, ±m n, l l±m l±m

$$\psi(r,\theta,\phi)_{n,l,l\pm m} = \sqrt{\left(\frac{2z}{na_0}\right)^3 \frac{4(n-l-1)!}{2n(n+l)^3}}\, e^{-\frac{p}{2}}.p^l.L_{n+l}^{2l+1}(p).\sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}}P_l^m \cos\theta.\frac{1}{\sqrt{2\pi}}e^{\pm im\phi}$$

6.3 Hydrogen like atom

The co-ordinates of electron of Helium atom can be represented as



Hamiltonian operator of Helium atom is

Unit -6 Quantum Mechanical Treatment

NOTE

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{1,2}} \quad \text{in au.}$$

For the ground state of Helium atom, the electronic configuration is $1s^2$. The overall wave function will be given by a slater determinant.

$$\psi_0 = \frac{1}{\sqrt{2}} 1S_{(1)}\overline{1S_{(2)}}$$

this on expansion may be written as

$$\psi_0 = \frac{1}{\sqrt{2}} 1S_{(1)} 1S_{(2)} [\alpha_{(1)} \beta_{(2)} - \beta_{(1)} \alpha_{(2)}]$$

According to variation method, the energy, E based on the approximate wave function is always higher than true energy E_o of the ground state.

$$E = \langle \psi_0 / H / \psi_0 \rangle$$

$$= \frac{1}{2} \langle 1S_{(1)} 1S_{(2)} | H | S_{(1)} / S_{(2)} | \rangle \langle \alpha_{(1)} \beta_{(2)} - \beta_{(1)} \alpha_{(2)} / \alpha_{(1)} \beta_{(2)} - \beta_{(1)} \alpha_{(2)} \rangle$$

$$= \frac{1}{2} \langle 1S_{(1)} 1S_{(2)} | H | S_{(1)} / S_{(2)} | \rangle . 2$$

$$E = \langle 1S_{(1)} 1S_{(2)} | H | S_{(1)} / S_{(2)} | \rangle$$

Hamiltonian for Helium atom is

$$H = H_{(1)} + H_{(2)} + \frac{1}{r_{1,2}} \quad 1S_{(1)} 1S_{(2)}$$

$$E = \left\langle 1S_{(1)} 1S_{(2)} \middle| H_{(1)} + H_{(2)} + \frac{1}{r_{1,2}} \middle| 1S_{(1)} 1S_{(2)} \right\rangle$$

$$E = \left\langle \langle | 1S_{(1)} 1S_{(2)} | H_{(1)} | 1S_{(1)} 1S_{(2)} | \rangle + \langle | 1S_{(1)} 1S_{(2)} | H_{(2)} | 1S_{(1)} 1S_{(2)} | \rangle + \langle | 1S_{(1)} 1S_{(2)} | \frac{1}{r_{1,2}} | 1S_{(1)} 1S_{(2)} | \rangle \right\rangle$$

NOTE

$$E = \langle 1S_{(1)} / H_{(1)} / 1S_{(2)} | \rangle \langle 1S_{(2)} | 1S_{(2)} | \rangle + | 1S_{(2)} / H_{(2)} / 1S_{(2)} | \rangle \langle 1S_{(1)} | 1S_{(1)} \rangle + J \rangle$$

$$E = E_{1S\,(1)} + E_{1S\,(2)} + J$$

$$J = \langle 1S_{(1)} \;\; /1S_2 | \rangle \left| \frac{1}{r_{1,2}} \right| 1S_{(1)} 1S_{(2)} | \rangle$$

J is called coulomb integral.

In a two electron atom, the average potential experienced by an electron varies between $-\frac{1}{r_i}$ and $-\frac{2}{r_i}$ that is it depends on the effective nuclear charge 'Z'. The best value of Z$'$ will be determined by the variation principle.

The wave function of 1S orbital appropriate to this effective nuclear charge Z$'$ is

$$1s = \frac{(Z')^{\frac{3}{2}}}{\sqrt{\pi}} . e^{-Z'r}$$

The result of calculation then leads to

$$E = -Z'^2 - 2(2 - Z')\, Z' + 5/8\, Z'$$

$$= Z'^2 - 27/8\, Z'$$

The value of Z′ which minimizes the energy is found by differentiating E with respect to Z′

Setting $\frac{\partial E}{\partial Z'} = 0$, we get

$$2Z' - \frac{27}{8} = 0$$

$$Z = \frac{27}{16} = 1.69$$

$$\therefore\; E = -2.8476 (a.u)$$

$$(1a.u = 27.2ev)$$

$$E = -77.48eV.$$

NOTE

6.4 Pauli's Exclusion Principle

Pauli's exclusion principle states that "The total wave function of electron must be antisymmetric under the interchange of any two electrons or no two electrons in one and the same orbitals can have all the fact quantum numbers same".

The four possible product combinations of the orbital and spin wave function for He atom in $1s^2$ state is

$$\left(1S_{(1)}1S_{(2)}\right)\left(\alpha_{(1)}/\alpha_{(2)}\right) \quad S\times S=S$$

$$\left(1S_{(1)}1S_{(2)}\right)\left(\beta_{(1)}/\beta_{(2)}\right) \quad S\times S=S$$

$$\left(1S_{(1)}1S_{(2)}\right)\frac{1}{\sqrt{2}}\left(\alpha_{(1)}\beta_{(2)}+\alpha_{(2)}\beta_{(1)}\right) \quad S\times S=S$$

$$\left(1S_{(1)}1S_{(2)}\right)\frac{1}{\sqrt{2}}\left(\alpha_{(1)}\beta_{(2)}-\alpha_{(2)}\beta_{(1)}\right) \quad S\times A=A$$

Symmetric (+) × symmetric (+) or

Antisymmetric (-) × Antisymmetric (-) is symmetric (+), but

Symmetric (+) × Antisymmetric (-) is Antisymmetric (-)

Complete description of an electron is given by the spin orbital wave function

$$\Psi(r, s) = \Phi(r)\, \eta(s)$$

$\Phi(r)$ is the orbital wave function, which is a function of the position variable and $\eta(s)$ is the spin function involving spin variable.

Spin orbital wave function is obtained by multipling each of the orbital function with those of the spin functions.

$$\Psi(r,s) = \Phi(r)\, \eta(s)$$

$$\psi = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)+\phi_2(1).\phi_1(2)\right)\left(\alpha_{(1)}.\alpha_{(2)}\right)$$

S×S = S

$$\psi = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)+\phi_2(1).\phi_1(2)\right)\left(\beta_{(1)}.\beta_{(2)}\right)$$

S×S = S

$$\psi = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)+\phi_2(1).\phi_1(2)\right).\left(\alpha_{(1)}\beta_{(2)}+\beta_{(1)}\alpha_{(2)}\right)$$

S×S = S

$$\psi = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)+\phi_2(1).\phi_1(2)\right).\left(\alpha_{(1)}\beta_{(2)}-\beta_{(1)}\alpha_{(2)}\right) \qquad S\times A = A$$

$$\psi = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)-\phi_2(1).\phi_1(2)\right)\left(\alpha_{(1)}.\alpha_{(2)}\right) \qquad A\times S = A$$

$$\psi = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)-\phi_2(1).\phi_1(2)\right)\left(\beta_{(1)}.\beta_{(2)}\right) \qquad A\times S = A$$

$$\psi = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)-\phi_2(1).\phi_1(2)\right).\left(\alpha_{(1)}\beta_{(2)}+\beta_{(1)}\alpha_{(2)}\right) \qquad A\times S = A$$

$$\psi = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)-\phi_2(1).\phi_1(2)\right).\left(\alpha_{(1)}\beta_{(2)}-\beta_{(1)}\alpha_{(2)}\right) \qquad A\times A = S$$

Of the eight possible combinations only four combinations are antisymmetric and they are accepted according to Pauli's exclusion principle.

$$\psi_A(r,s) = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)+\phi_2(1).\phi_1(2)\right).\left(\alpha_{(1)}\beta_{(2)}-\beta_{(1)}\alpha_{(2)}\right) \rightarrow (1)$$

$$\psi_A(r,s) = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)-\phi_2(1).\phi_1(2)\right)\left(\alpha_{(1)}.\alpha_{(2)}\right) \rightarrow (2)$$

$$\psi_A(r,s) = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)-\phi_2(1).\phi_1(2)\right)\left(\beta_{(1)}.\beta_{(2)}\right) \rightarrow (3)$$

$$\psi_A(r,s) = \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2)-\phi_2(1).\phi_1(2)\right).\left(\alpha_{(1)}\beta_{(2)}+\beta_{(1)}\alpha_{(2)}\right) \rightarrow (4)$$

To prove Pauli's exclusion principle consider equation (4)

NOTE

$$\psi_A(r,s) = \frac{1}{\sqrt{2}}(\phi_1(1).\phi_2(2) - \phi_2(1).\phi_1(2)).(\alpha_{(1)}\beta_{(2)} + \beta_{(1)}\alpha_{(2)})$$

This can be written in the Slater determinantal form.

$$= \frac{1}{\sqrt{2}}(\phi_1(1).\phi_2(2)\alpha_{(1)}\beta_{(2)} + \phi_1(1).\phi_2(2)\beta_{(1)}\alpha_{(2)} - \phi_2(1).\phi_1(2)\alpha_{(1)}\beta_{(2)} - \phi_2(1).\phi_1(2)\beta_{(1)}\alpha_{(2)})$$

$$= \frac{1}{\sqrt{2}}\left(\phi_1(1).\phi_2(2) + \phi_1(1).\phi_2(2) - \phi_2(1).\phi_1(2) - \phi_2(1).\phi_1(2)\right)$$

$$\psi_A(r,s) = \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(1) & \phi_2(1)\\ \phi_1(2) & \phi_2(2)\end{vmatrix} + \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(1) & \phi_1(2)\\ \phi_2(1) & \phi_2(2)\end{vmatrix}$$

When both the electrons are in the same orbitals

$\Phi_1 = \Phi_2$. Therefore the determinant becomes

$$\psi_A(r,s) = \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(1) & \phi_1(1)\\ \phi_1(2) & \phi_1(2)\end{vmatrix} + \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(1) & \phi_1(2)\\ \phi_1(1) & \phi_1(2)\end{vmatrix}$$

when α = β

$$\psi_A(r,s) = \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(1) & \phi_1(1)\\ \phi_1(2) & \phi_1(2)\end{vmatrix} + \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(1) & \phi_1(2)\\ \phi_1(1) & \phi_1(2)\end{vmatrix}$$

When two rows of the determinant or two columns of a determinant are equal then the determinant vanishes i.e. it is equal to zero. The wave function also vanishes. Hence no two electrons in one and the same orbital can have all the four quantum numbers same. Pauli's exclusion principle is proved.

6.5 Slater determinant

In order to construct antisymmetric wave function for a multi-electron atom, the increase in the number of electrons increases the number of terms in such large proportions [for ex: 5! i.e 120 terms for an atom with 5 electrons only]. We must find an abbreviated form to represent a wave function. This can be done by writing it in the form a determinant in which the spin-orbitals are the elements, each row in the determinant is labeled with an electron and each column with a spin orbital.

The normalized wave function for a three electron atom is written as

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} A_{(1)} & B_{(1)} & C_{(1)} \\ A_{(2)} & B_{(2)} & C_{(2)} \\ A_{(3)} & B_{(3)} & C_{(3)} \end{vmatrix} \rightarrow (1)$$

For an n electron atom

$$\psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} A_{(1)} & B_{(1)} & \cdots\cdots \\ A_{(2)} & B_{(2)} & \cdots\cdots \\ A_{(n)} & B_{(n)} & \cdots\cdots \end{vmatrix} \rightarrow (2)$$

The antisymmetry of equation (1) or equation (2) as well as Pauli's principle are guaranteed by two properties of determinants.

(1) If two rows (or) two columns of a determinant are interchanged , the resulting
determinant is just the negative of the original one, i.e

NOTE

$$\begin{vmatrix} A_{(1)} & B_{(1)} & C_{(1)} \\ A_{(2)} & B_{(2)} & C_{(2)} \\ A_{(3)} & B_{(3)} & C_{(3)} \end{vmatrix} = - \begin{vmatrix} A_{(2)} & B_{(2)} & C_{(2)} \\ A_{(1)} & B_{(1)} & C_{(1)} \\ A_{(3)} & B_{(3)} & C_{(3)} \end{vmatrix}$$

(2) If any two rows or two columns of a determinant are the same, the determinant vanishes.

For example:

The ground state antisymmetric wave function for He atom in the determinantal form and to prove that the two electrons cannot have the same spin-orbital.

$$\psi_- = |1S_{(1)}1S_{(2)}|(\alpha_{(1)}\beta_{(2)} - \alpha_{(2)}\beta_{(1)})$$

$$= |1S_{(1)}\alpha_{(1)}.1S_{(2)}\beta_{(2)}| - |1S_{(1)}\beta_{(1)}.1S_{(2)}\alpha_{(2)}|$$

$$= \begin{vmatrix} 1S_{(1)}\alpha_{(1)} & 1S_{(1)}\beta_{(1)} \\ 1S_{(2)}\alpha_{(2)} & 1S_{(2)}\beta_{(2)} \end{vmatrix} \rightarrow (3)$$

where $1S_{(i)}\alpha_{(i)}$ is the spin-orbital of electron i (i = 1, 2)

If both electrons have the same spin-orbitals, the determinant

$$= \begin{vmatrix} 1S_{(1)}\alpha_{(1)} & 1S_{(1)}\alpha_{(1)} \\ 1S_{(2)}\alpha_{(2)} & 1S_{(2)}\alpha_{(2)} \end{vmatrix} = 0$$

With increasing number of electrons, even the determinant (2) will have large size and further abbreviation is necessary. This is done by using a bar over the orbital which has β spin,

absence of a bar will indicate α spin. Thus the determinant wave function for Li atom is

$$\psi = \frac{1}{\sqrt{3!}}\begin{vmatrix} 1S_{(1)} & \overline{1S_{(1)}} & 2S_{(1)} \\ 1S_{(2)} & \overline{1S_{(2)}} & 2S_{(2)} \\ 1S_{(3)} & \overline{1S_{(3)}} & 2S_{(3)} \end{vmatrix}$$

NOTE

6.6 Approximation methods

Need for approximation methods:

1. Schrodinger wave equation cannot be solved exactly in many electron atoms because the presence of more than one electron introduces electron repulsion terms (e^2/r_{ij}), where r_{ij} is the distance between the two electrons. This r_{ij} term depends on ϕ and θ coordinates. The separation of variables is not possible and is very difficult.

2. Again the Schrodinger wave equation cannot be solved exactly for one electron systems, whose potential field is not spherically symmetrical e.g. Hydrogen atom subjected to electric or magnetic field.

Hence to obtain the solution of the wave equation for the above systems approximate methods are used. The two commonly used methods are

(i) Variation method

(ii) Perturbation method

6.7 Variation Method

Variation method is an approximation method. It is used to those systems, which differ much from the systems, for which exact solution is known. In this system the wave functions can be guessed based on physical and chemical combinations and the energy of the system is calculated by

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$$ when ψ is normalized, then

$E = \langle\psi|H|\psi\rangle$ where $\hat{H}$ is the complete Hamiltonian of the system.

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NOTE

Variation theorem states that "if ψ be the normalized trial wave function satisfying the boundary conditions of a system, whose Hamiltonian $\hat{H}$ has a discrete eigen spectrum".

Then

$$\langle \psi | H | \psi \rangle \geq E_0$$

where E_0 is the lowest exact Eigen value of $\hat{H}$.

The wave function ψ is called trial variational function and the integral $\langle \psi | H | \psi \rangle$ is called the variational integral. The energy calculated by variation method will always be greater than the true energy E_0 i.e. the lowest eigen value of $\hat{H}$.

Proof of variation theorem i.e. proof for $\langle \psi | H | \psi \rangle \geq E_0$

Let $\phi_0, \phi_1, \phi_2, \phi_3$…..be the set of normalized and mutually orthogonal eigen functions of $\hat{H}$ with discrete eigen values E_0, E_1, E_2, E_3 ,etc. such that

$$H\phi_i = E_i\phi_i \qquad i = 0, 1, 2, 3…..$$

Let ψ be a normalized trial variational function. Let ψ be expanded in terms of the orthogonal set of functions i.e. $\psi = \sum_i C_i\phi_i$

Multiply by ψ^* and integrate over all space,

$$\langle \psi | \psi \rangle = \left\langle \sum_i C_i\phi_i \middle| \sum_i C_i\phi_i \right\rangle$$

$$= \sum_i C_i^2 \langle \phi_i | \phi_i \rangle$$

$$\langle \psi | \psi \rangle = \sum_i C_i^2 = 1 \qquad [\because \psi \text{ is normalized } \langle \psi | \psi \rangle = 1]$$

Considering the variational integral

$$E = \langle \psi | H | \psi \rangle$$

$$E = \left\langle \sum_i C_i\phi_i \middle| H \middle| \sum_j C_j\phi_j \right\rangle$$

$$E = \langle C_1\phi_1 + C_2\phi_2 + C_3\phi_3 + \ldots | H | C_1\phi_1 + C_2\phi_2 + C_3\phi_3 + \ldots \rangle$$

$$E = \sum_i C_i^2 \langle \phi_i | H | \phi_i \rangle + \sum_{i \neq j} C_{ij} \langle \phi_i | H | \phi_j \rangle \rightarrow (1)$$

Moreover, $\langle \phi_i | H | \phi_i \rangle = E_i \rightarrow (a)$

$$\langle \phi_i | H | \phi_j \rangle = E_j \langle \phi_i | \phi_j \rangle = 0 \rightarrow (b)$$

Then (1) becomes

$E = \sum_i C_i^2 E_i + 0$ [The second summation in (1) vanishes due to (b)]

If E_0 is the energy of the lowest state or lowest Eigen value of $\hat{H}$ then

$$E - E_0 = \sum_i C_i^2 E_i - \sum_i C_i^2 E_0 \quad [\because \sum_i C_i^2 = 1]$$

$$E - E_0 = \sum_i C_i^2 (E_i - E_0) \rightarrow (2)$$

The quantity $E_i - E_0$ must be positive or zero for all values of i and C_i^2 is always positive, the R.H.S of the above equation (2) must always be positive or zero.

Hence $E - E_0 \geq 0$

$$E \geq E_0$$

$$\langle \psi | H | \psi \rangle \geq E_0$$

This is variation theorem.

6.8 Time Independent Perturbation

Perturbation method is an approximation method used to solve the wave equations representing the systems having more than one electron. This method is suitable for a system, which are subjected to very weak

electric or magnetic field and also for the system whose zero order states are non-degenerate.

Conditions under which perturbation theory is based:

1. The total Hamiltonian of the perturbed system is the sum of the parts (i)unperturbed Hamiltonian $\hat{H}^{(0)}$ and (ii) perturbation

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{V}$$

where $\lambda\hat{V}$ is the perturbation and λ is the expansion parameter.

2. The system is only very slightly disturbed and different from the system for which the exact solution is known i.e. $\lambda\hat{V}$ is very small compared to $\hat{H}^{(0)}$.

$$\hat{H}^{(0)} \rangle\rangle \lambda\hat{V}$$

3. The eigen values $E^{(0)}$ and eigen functions $\psi^{(0)}$ of the unperturbed Hamiltonian $H^{(0)}$ are known.

$$H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$$

4. If ψ is the wave function of the Hamiltonian of the perturbed system $\hat{H}$ with eigen value E then the eigen value equation is

$$\hat{H}\psi = E\psi$$

$$(H^{(0)} + \lambda\hat{V})\psi = E\psi$$

The wave function ψ and energy E are functions of λ and hence it is possible to expand them in terms of λ in the form of power series as

$$\psi = \psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \lambda^3\psi^{(3)} + \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

And

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \quad (2)$$

Where $\psi^{(1)}, \psi^{(2)}$...... and $E^{(1)}, E^{(2)}$ …. Etc are independent of λ. $\psi^{(1)} and\, \psi^{(2)}$ are chosen such that they are orthogonal to $\psi^{(0)}$, which is normalized.

5. The equation of the perturbed system is

$$(H^0+\lambda\hat{V})(\psi^{(0)}+\lambda\psi^{(1)}+\lambda^2\psi^{(2)}+...)=(E^0+\lambda E^{(1)}+\lambda^2E^{(2)}+....)(\psi^{(0)}+\lambda\psi^{(1)}+\lambda^2\psi^{(2)}+...)$$

The order of accuracy depends on the number of terms chosen in the above equation. Since the perturbed system is only slightly different from the unperturbed one. $\psi^{(0)}$ and $E^{(0)}$ may be chosen as approximate solutions of the perturbed system. This is called zeroth order approximation to the true solution of the perturbed system.

If the second term in the series that is $\psi=\psi^{(0)}+\lambda\psi^{(1)}$ and $E=E^{(0)}+\lambda E^{(1)}$ are chosen and the schrodinger wave equation is solved it will give rise to first order approximation to the true solution of the perturbed system.

$\hat{H}^{(0)}\psi^{(0)}=E^{(0)}\psi^{(0)}\rightarrow$ Zeroth order perturbation equation.

$\left(\hat{H}^{(0)}-E^{(0)}\right)\psi^{(1)}=-\hat{V}\psi^{(0)}+E^{(1)}\psi^{(0)}\rightarrow$ First order perturbation equation.

First order perturbation theory:

First order perturbation equation is

$$\left(\hat{H}^{(0)}-E^{(0)}\right)\psi^{(1)}=-\hat{V}\psi^{(0)}+E^{(1)}\psi^{(0)}$$

By solving this equation first order correction to the eigen function $\psi^{(1)}$ and the first order correction to the eigen value $E^{(1)}$ are obtained then ψ and E are calculated.

$$\psi=\psi^{(0)}+\lambda\psi^{(1)}$$

$$E=E^{(0)}+\lambda E^{(1)}$$

$\psi^{(0)}$ and $E^{(0)}$ are known for the given system under consideration.

First order correction to the energy and approximate energy of the perturbed system:

NOTE

$\left(\hat{H}^{(0)} - E_i^{(0)}\right)\psi_i^{(1)} = -\hat{V}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(0)}$ is the first order perturbation equation for the i[th] state . $\psi_i^{(1)}$ is expanded in terms of the complete set of eigen functions of the unperturbed Hamiltonian $H^{(0)}$. The unperturbed equation is

$$\hat{H}^{(0)}\psi_i^{(0)} = E_i^{(0)}\psi_i^{(0)}$$

where i = 0,1,2,3 etc.

$\psi_0^{(0)}\psi_1^{(0)}\psi_2^{(0)}.......\psi_i^{(0)}\psi_j^{(0)}$ etc belong to orthonormal set of functions and $E_i^{(0)}$ is non-degenerate.

$$\psi_i^{(1)} = \sum_{j\neq i} C_{ij}\psi_j^{(0)} \rightarrow (a)$$

Multiply by $\psi_1^{(0)}$ and integrate over all space

$$\left\langle \psi_i^{(0)} \middle| \psi_i^{(1)} \right\rangle = \sum_{j\neq i} C_{ij} \left\langle \psi_i^{(0)} \middle| \psi_j^{(0)} \right\rangle = 0$$

Since the wave function $\psi_i^{(0)}$ is orthogonal to $\psi_j^{(0)}$. Hence $\psi_i^{(0)}$ is orthogonal to $\psi_j^{(1)}$.

Substituting the value of $\psi_j^{(1)}$ in the first order perturbation equation we get

$$\left(\hat{H}^0 - E_i^{(0)}\right)\sum_{j\neq i} C_{ij}\psi_j^{(0)} = -\hat{V}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(0)}$$

$$\sum_{j\neq i} C_{ij}[\hat{H}^0 - E_i^{(0)}\psi_j^{(0)}] = -\hat{V}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(0)}$$

$$H^{(0)}\psi_j^{(0)} = E_j^{(0)}\psi_j^{(0)}$$

$$\sum_{j\neq i} C_{ij}(E_j^{(0)} - E_i^{(0)})\psi_j^{(0)} = -\hat{V}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(0)}$$

Multiply by $\psi_i^{(0)}$ and integrate over all space

$$\sum_{j\neq i} C_{ij}\langle\psi_i^{(0)}|E_j^{(0)} - E_i^{(0)}|\psi_j^{(0)}\rangle = -\langle\psi_i^{(0)}|\hat{V}|\psi_i^{(0)}\rangle + E_i^{(1)}\langle\psi_i^{(0)}|\psi_i^{(0)}\rangle$$

$$\sum_{j\neq i} C_{ij}(E_j^{(0)} - E_i^{(0)})\langle\psi_i^{(0)}|\psi_j^{(0)}\rangle = -\langle\psi_i^{(0)}|\hat{V}|\psi_i^{(0)}\rangle + E_i^{(1)}\langle\psi_i^{(0)}|\psi_i^{(0)}\rangle$$

$\psi_i^{(0)}$ and $\psi_j^{(0)}$ etc belong to orthonormal set. Hence

$$\langle\psi_i^{(0)}|\psi_j^{(0)}\rangle = 0 \text{ and } \langle\psi_i^{(0)}|\psi_i^{(0)}\rangle = 1$$

$$0 = -\langle\psi_i^{(0)}|\hat{V}|\psi_i^{(0)}\rangle + E_i^{(1)}$$

$$E_i^{(1)} = \langle\psi_i^{(0)}|\hat{V}|\psi_i^{(0)}\rangle$$

Hence first order correction to the energy of the i^th state is

$$E_i^{(1)} = \langle\psi_i^{(0)}|\hat{V}|\psi_i^{(0)}\rangle$$

$E_i^{(1)}$ is the first order correction to the true energy. The approximate energy of the perturbed system according to the non-degenerate time independent first order perturbation theory is

$$E_i = E_i^{(0)} + \lambda E_i^{(1)}$$

$$E_i = E_i^{(0)} + \lambda\langle\psi_i^{(0)}|\hat{V}|\psi_i^{(0)}\rangle$$

First order correction to the wave function:

First order perturbed equation for the i^th state is

NOTE

$$\left(\hat{H}^0 - E_i^{(0)}\right)\psi_i^{(1)} = -V\psi_i^0 + E_j^{(1)}\psi_i^0$$

NOTE

$\psi_i^{(1)}$ is expanded in terms of a complete set of eigen functions of the unperturbed Hamiltonian

$$\psi_i^{(1)} = \sum_{j \neq i} C_{ij}\psi_j$$

$\psi_i^{(0)}$ and $\psi_j^{(0)}$ belong to orthonormal set. Substituting this in perturbation equation

$$\left(\hat{H}^0 - E_i^{(0)}\right)\sum_{j\neq i} C_{ij}\psi_j^{(0)} = -\hat{V}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(0)}$$

$$H^{(0)}\psi_j^{(0)} = E_j^{(0)}\psi_j^{(0)}$$

$$\sum_{j \neq i} C_{ij}(E_j^{(0)} - E_i^{(0)})\psi_j^{(0)} = -\hat{V}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(0)}$$

upon expanding the summation we get,

put j = 1, 2, 3, 4 ....for the i[th] state.

$$C_{i1}(E_1^{(0)} - E_i^{(0)})\psi_1^{(0)} + C_{i2}(E_2^{(0)} - E_i^{(0)})\psi_2^{(0)} + C_{i3}(E_3^{(0)} - E_i^{(0)})\psi_3^{(0)} + C_{i4}(E_4^{(0)} - E_i^{(0)})\psi_4^{(0)} + ...$$
$$= -\hat{V}\psi_i^{(0)} + E_i^{(1)}\psi_i^{(0)}$$

In order to obtain C_{i1} multiply both sides by $\psi_1^{(0)}$ and integrated over all space

$$(E_1^{(0)} - E_i^{(0)})C_{i1}\langle\psi_1^{(0)}|\psi_1^{(0)}\rangle = -\langle\psi_1^{(0)}|\hat{V}|\psi_i^{(0)}\rangle + E_i^{(1)}\langle\psi_1^{(0)}|\psi_i^{(0)}\rangle$$

NOTE

Since the zero order wave functions are orthogonal and individually normalized

$$\langle \psi_1^{(0)} | \psi_1^{(0)} \rangle = 1 \qquad \langle \psi_1^{(0)} | \psi_i^{(0)} \rangle = 0 \qquad 1 \neq i$$

$$C_{i1} = \frac{-\langle \psi_1^{(0)} | \hat{V} | \psi_i^{(0)} \rangle}{(E_{1i}^{(0)} - E^{(0)})}$$

$$C_{i2} = \frac{-\langle \psi_2^{(0)} | \hat{V} | \psi_i^{(0)} \rangle}{(E_{2i}^{(0)} - E^{(0)})}$$

$$C_{ij} = \frac{-\langle \psi_j^{(0)} | \hat{V} | \psi_i^{(0)} \rangle}{(E_j^{(0)} - E_i^{(0)})}$$

$$C_{ij} = \frac{+\langle \psi_j^{(0)} | \hat{V} | \psi_i^{(0)} \rangle}{(E_j^{(0)} - E_i^{(0)})}$$

Substituting the value of C_{ij} in $\psi_i^{(1)}$

$$\psi_i^{(1)} = \sum_{i \neq j} \frac{\langle \psi_j^{(0)} | \hat{V} | \psi_i^{(0)} \rangle}{(E_j^{(0)} - E_i^{(0)})} . \psi_j^{(0)}$$

$\psi_i^{(1)}$ is the first order correction to the true value function.

$$E_j^{(0)} \neq E_i^{(0)}$$

Thus according to the non-degenerate time independent first order perturbation theory.

Approximate solution of the first order perturbation equation.

$$\psi_i = \psi_i^{(0)} + \lambda \sum_{i \neq j} \frac{\langle \psi_j^{(0)} | \hat{V} | \psi_i^{(0)} \rangle}{(E_j^{(0)} - E_i^{(0)})} . \psi_j^{(0)}$$

NOTE

This relationship is not valid if there is degeneracy in the eigen spectrum of $H^{(o)}$ that is $E_j - E_i$ for $i \neq j$. For it to be valid ground state should be non-degenerate.

6.9 SCE Methods

According to Hartree each electron is assumed to move in a spherically symmetrical field due to the nucleus and the average potential field is due to all the electrons except the one under consideration. This field in which electron move is called self consistent field.

The wave function of an atom containing 'n' electrons is written as product of 'n' number of one electron functions that is

$$\psi = \phi_1(1)\phi_2(2)\phi_3(3) \quad \phi_n(n)$$

where ϕ_1, ϕ_2, ϕ_3 .... ϕ_n are the normalized and mutually orthogonal one electron wave functions.

$\phi_1(1)$ means the electron (1) is put in the orbital ϕ_1................ etc.

The antisymmetric wave function of the atom is expressed as a determinant.

$$\psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1) & \overline{\phi_1(1)} & \phi_2(1) & \overline{\phi_2(1)} & \cdots & \overline{\phi_{\frac{n}{2}}(1)} \\ \phi_1(2) & \overline{\phi_1(2)} & \phi_2(2) & \overline{\phi_2(2)} & \cdots & \overline{\phi_{\frac{n}{2}}(2)} \\ \vdots & & & & \cdots & \\ \phi_1(n) & \overline{\phi_1(n)} & \phi_2(n) & \overline{\phi_2(n)} & \cdots & \overline{\phi_{\frac{n}{2}}(n)} \end{vmatrix}$$

For an n-electron atom with closed shell configuration, that is in which all atomic orbitals are doubly occupied with paired spins.

$$\psi = \frac{1}{\sqrt{n!}}\left| \phi_1(1) \quad \overline{\phi_1(2)} \quad \phi_2(3) \quad \overline{\phi_2(4)} \quad \ldots\ldots\ldots \quad \overline{\phi_{\frac{n}{2}}(n)} \right|$$

where the determinant has been represented through diagonal elements. $\phi_1(1)$ is the spin orbital with electron 1, $\phi_2(2)$ with electron 2, in the same orbital ϕ, and so on.

Fock introduced a new operator $\hat{F}$ known as Fock operator. It is an operator for kinetic energy of electron, potential energy of inter electron repulsion and potential energy of electron spin exchange between pair of electrons.

The Fock operator for electron is defined as

$$\hat{F}_{(1)} = -\frac{1}{2}\nabla_1^2 - \frac{z}{r_1} + \sum_{j=1}^{n/2}\left(2J_j - K_j\right)$$

$-\frac{1}{2}\nabla_1^2$ represents kinetic energy operator for electron

$-\frac{z}{r_1}$ represents operator for potential energy of attraction between electron 1 and nucleus.

J_j represents operator for potential energy of repulsion between electron 1 and jth electron.

K_j represents operator for potential energy of change of spin between electron 1 and jth electron.

The potential energy of repulsion experienced by electron 1 in the field of electron j is given by the following operator J_j

$$J_j = \int \phi_j \frac{1}{r_{i,j}} \phi_j \, d\tau_j$$

The sum of the operator for the potential energy of repulsion experienced by electron 1 in a field of every other electron of the atom is expressed as follows

$$\sum_{j=1}^{n} J_j = \sum_{j=1}^{n} \int \phi_j \frac{1}{r_{i,j}} \phi_j \, d\tau_j$$

The potential energy of exchange of spin between electron 1 and electron j is given by the following operator K_1

$$K_1 = \int \phi_j \frac{1}{r_{1,j}} \phi_j d\tau_j$$

There will be exchange of spin between electron 1 and n/2 number of electron with opposite sign. Therefore there will be n/2 number of such operators. The sum of these operator is $\sum_{j=1}^{\frac{n}{2}} K_j$

$$\sum_{j=1}^{\frac{n}{2}} K_j = \sum_{j=1}^{\frac{n}{2}} \int \phi_j \frac{1}{r_{1,2}} \phi_j \, d\tau_j$$

Thus the Fock operator for electron 1 $\hat{F}_{(1)}$ is described. Similarly the Fock operator for other electrons can also be formed.

A set of orbitals without spin, $\phi_1, \phi_2, \phi_3 .... \phi_{\frac{n}{2}}$ with variable parameter in each is chosen. Using these functions, a set of Fock operators $\hat{F}_{(1)}, \hat{F}_{(2)}, \hat{F}_{(3)}, \hat{F}_{(4)} .... \hat{F}_{\frac{n}{2}}$ were formed. Substituting the above wave function with respective

Fock operators and so having the following “Pseudo-Schrodinger wave equation”. A set of wave functions $\phi_1',\phi_2',\phi_3'\text{............}\phi_{\frac{n}{2}}'$ were obtained

$$\hat{F}\phi_i = E_i\phi_i$$

Using the new set of wave functions, a new set of Fock operators $\hat{F}_{(1)}', \hat{F}_{(2)}', \hat{F}_{(3)}', \hat{F}_{(4)}' \ldots\ldots\ldots\ldots \hat{F}_{\frac{n}{2}}'$ are formed and using $\phi_1',\phi_2',\phi_3'\text{............}\phi_{\frac{n}{2}}'$, the pseudo schrodinger equation is solved to get a set of functions $\phi_1'',\phi_2'',\phi_3''\text{............}\phi_{\frac{n}{2}}''$. This process is repeated till we get a set of orbitals which are not very different from the previous set. This set of orbital is called self consistent field (SCF) orbitals $\phi_1^s,\bar{\phi}_1^s,\phi_2^s,\bar{\phi}_2^s$ …..

6.10 Check Your Progress

1. State Pauli’s exclusion principle
2. What is meant by Slater determinant?
3. Write notes on self consistent field method .

6.11 Answers to check your progress questions

1. Pauli’s exclusion principle states that “The total wave function of *electron must be antisymmetric under the interchange of any two* electrons or no two electrons in one and the same orbitals can have all the fact quantum numbers same”.

2. In order to construct antisymmetric wave function for a multi-electron atom, the increase in the number of electrons increases the number of terms in such large proportions [for ex: 5! i.e 120 terms for an atom with 5 electrons only]. We must find an abbreviated form to represent a wave function. This can be done by writing it in the form a determinant in which the spin-orbitals are the elements, each row in the determinant is labeled with an electron and each column with a spin orbital.

NOTE

3. According to Hartree each electron is assumed to move in a spherically symmetrical field due to the nucleus and the average potential field is due to all the electrons except the one under consideration. This field in which electron move is called self consistent field.

6.12 Summary

- Pauli's exclusion principle states that "The total wave function of electron must be antisymmetric under the interchange of any two electrons or no two electrons in one and the same orbitals can have all the fact quantum numbers same".
- For many problems, it is not practical to obtain a wave function by the exactsolution of a wave equation that describes the system. It is still possible toperform many types of calculations, and one of the most useful techniques is that known as the variation method.
- The exact solution of the Schrödinger wave equation for complex atomsis not possible. However, examination of the form of the wave functions obtained for the hydrogen atom suggests that approximate wave functionsmight be obtained if we were to take into account the mutual electronrepulsion. Such a procedure has been devised by J. C. Slater, and theapproximate wave functions that result are known as Slater wave functions [or Slater-type orbitals (STO)].
- Perturbation method is an approximation method used to solve the wave equations representing the systems having more than one electron. This method is suitable for a system, which are subjected to very weak electric or magnetic field and also for the system which zero order states are non-degenerate.
- According to Hartree each electron is assumed to move in a spherically symmetrical field due to the nucleus and the average potential field is due to all the electrons except the one under consideration. This field in which electron move is called self consistent field.

6.13 Keywords

- **Radial wave function:** An orbital in a mathematical function called a wave function that describes an electron in an atom.Radial wave function for a given atom depend only upon the distance, r from the nucleus.
- **Angular wave function**: Angular wave functions depend only upon direction and in effect, describes the shape of an orbital.

- **Petrubation**: The act of disturbance, in physics a secondary influence on a system that modifies simple behaviour, such as the effect of the other electrons on one electron in an atom.

6.14 Self-assessment questions and exercises

1. Discuss the principle of variation method.
2. What is meant by Slater determinant? Obtain its value for helium atom.
3. "For many electron systems only approximation methods are needed"- Explain.

6.15 Further readings

1. **Quantum Chemistry**, I.N. Levine, Allyn and Bacon, Boston, 1983.
2. **Quantum Chemistry**, R.K.Prasad, Wiley Eastern, New Delhi,1992.

UNIT- 7 HMO Method

Structure

7.0 Introduction

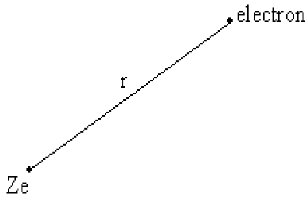
when the phrase "molecular orbital calculations" is first encountered,
the mental image may well be one of hopelessly complicated mathematics and piles upon piles of computer output. It is interesting to note, however, that sometimes a relatively simple calculation may provide useful information that correlates well with experimental observations. Such is the case with the method known as the Hückel molecular orbital (HMO theory) calculation. This method was developed in 1931 by Erich Hückel, a physicist in Marburg, Germany, who was trying to understand the concept of aromaticity in benzene. The calculational procedures are relatively simple and have become known as the "back of an envelope" calculations.

7.1 Objectives

After going through this unit, you will be able to:

- Explain about the application of variation methods to hyderogen atom.
- Understand the concept of HMO method and application to butadiene.

7.2 Application of Perturbation method to hydrogenatom



Hamiltonian operator of Hydrogen atom in atomic units

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Hydrogen atom is spherically symmetrical and hence the wave function has no nodes and ψ is independent of θ and Φ.

Hence $\quad \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}$

And Hamiltonian $\quad H = \left(-\frac{1}{2}\left(\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\right) - \frac{1}{r}\right)$

The wave function for hydrogen atom is chosen by infinitive means. Let

$$\psi = e^{-ar}$$

where ‘a’ is the variable parameter.

The energy of the system is obtained from the variational integral.

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

NOTE

$$E = \frac{\left\langle e^{-ar} \middle| -\frac{1}{2}\left(\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}\right) - \frac{1}{r} \middle| e^{-ar} \right\rangle}{\left\langle e^{-ar} \middle| e^{-ar} \right\rangle}$$

$$E = \frac{\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{-ar}\left(-\frac{1}{2r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} e^{-ar} - \frac{1}{r}e^{-ar}\right) r^2 \sin\theta dr d\theta d\phi}{\int_0^\infty\int_0^\pi\int_0^{2\pi} e^{-ar}.e^{-ar}.r^2 \sin\theta dr d\theta d\phi}$$

$$E = \frac{\int_0^\infty e^{-ar}\left[-\frac{1}{2r^2}\left(\frac{\partial}{\partial r} r^2 e^{-ar}.(-a)\right) - \frac{e^{-ar}}{r}\right] r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi}{\int_0^\infty e^{-2ar}.r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi}$$

$$E = \frac{\int_0^\infty e^{-ar}\left[\frac{a}{2r^2}\left(r^2 e^{-ar}.(-a) + e^{-ar}.2r\right) - \frac{e^{-ar}}{r}\right] r^2 dr}{\int_0^\infty e^{-2ar}.r^2 dr}$$

$$E = \frac{\int_0^\infty e^{-ar}\left[\left(-\frac{a^2}{2}e^{-ar} + a.\frac{e^{-ar}}{r}\right) - \frac{e^{-ar}}{r}\right] r^2 dr}{\int_0^\infty e^{-2ar}.r^2 dr}$$

$$E = \frac{\int_0^\infty -\frac{a^2}{2} e^{-2ar} r^2 dr + \int_0^\infty a.e^{-2ar}.r dr - \int_0^\infty e^{-2ar}.r dr}{\int_0^\infty e^{-2ar}.r^2 dr}$$

$$E = \frac{-\frac{a^2}{2}\int_0^\infty e^{-2ar} r^2 dr + a\int_0^\infty e^{-2ar}.r dr - \int_0^\infty e^{-2ar}.r dr}{\int_0^\infty e^{-2ar}.r^2 dr}$$

$$E = \frac{-\frac{a^2}{2}\cdot\frac{2!}{(2a)^{2+1}} + a\cdot\frac{1!}{(2a)^{1+1}} - \frac{1!}{(2a)^{1+1}}}{\frac{2!}{(2a)^{2+1}}}$$

$$E = \frac{-\frac{1}{8a} + \frac{1}{4a} - \frac{1}{4a^2}}{\frac{2}{8a^3}} = \frac{\left(-a + 2a - 2\right) 8a^3}{8a^2 \cdot 2}$$

$$E = \frac{a^2 - 2a}{2}$$

Energy is minimized with respect to a

$$\frac{\partial E}{\partial a} = 0$$

$$\frac{\partial}{\partial a}\left(\frac{a^2 - 2a}{2}\right) = \frac{1}{2}(2a - 2) = 0$$

$$a = 1$$

Hence the wave function is

$$\psi = e^{-r}$$

Energy

$$E = \frac{a^2 - 2a}{2}$$

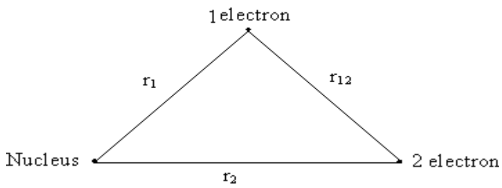
$$E = \frac{1 - 2}{2} = -\frac{1}{2}\,au$$

This represents the exact value of energy and exact eigen function for hydrogen atom in its ground state. Any other wave function chosen will always lead to an energy greater than the lowest exact energy of the system.

7.3 Application of Perturbation Method to Helium

The coordinates of electrons of Helium atom can be represented as

NOTE



Hamiltonian operator of Helium atom is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \text{ in au}$$

$$H = H_{(1)} + H_{(2)} + \frac{1}{r_{12}}$$

where $H_{(1)}$ and $H_{(2)}$ are the one electron hydrogen like Hamiltonians of the system.

For the ground state of Helium atom the electronic configuration is $1s^2$.

Slater determinantal form of overall wave function of Helium atom is

$$\psi_o = \psi_{1s}(1,2) = \psi_{1s}(He) = \frac{1}{\sqrt{2}}\left|1S_{(1)}\overline{1S}_{(2)}\right|$$

$$= \frac{1}{\sqrt{2}}\left(1S_{(1)}\,1S_{(2)}\right)\left(\alpha_{(1)}\beta_{(2)} - \beta_{(1)}\alpha_{(2)}\right)$$

This is the trial approximate wave function. According to variation method the energy based on the approximate wave function is always higher than the true energy E_o of the ground state.

$$E = \langle \psi_o | H | \psi_o \rangle$$

$$E_{1S} = \left\langle \frac{1}{\sqrt{2}} \left(1S_{(1)}1S_{(2)}\right)\left(\alpha_{(1)}\beta_{(2)} - \beta_{(1)}\alpha_{(2)}\right) \middle| H \middle| \frac{1}{\sqrt{2}} \left(1S_{(1)}1S_{(2)}\right)\left(\alpha_{(1)}\beta_{(2)} - \beta_{(1)}\alpha_{(2)}\right) \right\rangle$$

$$E_{1S} = \frac{1}{2} \left\langle \left(1S_{(1)}1S_{(2)}\right) \middle| H \middle| \left(1S_{(1)}1S_{(2)}\right) \left(\alpha_{(1)}\beta_{(2)} - \beta_{(1)}\alpha_{(2)}\right) \right\rangle$$

$$= \frac{1}{2} \left(1S_{(1)}1S_{(2)}\right) \middle| H \middle| \left(1S_{(1)}1S_{(2)}\right).2$$

$$= \left\langle \left(1S_{(1)}1S_{(2)}\right) \middle| H \middle| \left(1S_{(1)}1S_{(2)}\right) \right\rangle$$

Hamiltonian for Helium atom is

$$H = H_{(1)} + H_{(2)} + \frac{1}{r_{12}}$$

$$E_{1S} = \left\langle \left(1S_{(1)}1S_{(2)}\right) \middle| H_{(1)} + H_{(2)} + \frac{1}{r_{12}} \middle| \left(1S_{(1)}1S_{(2)}\right) \right\rangle$$

$$E_{1S} = \left\langle \left(1S_{(1)}1S_{(2)}\right) \middle| H_{(1)} \middle| \left(1S_{(1)}1S_{(2)}\right) + \left(1S_{(1)}1S_{(2)}\right) \middle| H_{(2)} \middle| \left(1S_{(1)}1S_{(2)}\right)\left(1S_{(1)}1S_{(2)}\right) \middle| \frac{1}{r_{12}} \middle| \left(1S_{(1)}1S_{(2)}\right) \right\rangle$$

$$E_{1S} = \left\langle \left(1S_{(1)} \middle| H_{(1)} \middle| 1S_{1}\right) \right\rangle \left\langle \left(1S_{(2)}1S_{(2)}\right) \right\rangle + \left(1S_{(21)} \middle| H_{(2)} \middle| 1S_{(2)}\right)\left(1S_{(1)}1S_{(1)}\right) + J \right\rangle$$

$$E_{1S} = E_{1S\,(1)} + E_{1S\,(2)} + J$$

$E_{1S\,(i)}$ is the energy of i[th] electron in the 1S orbital of Helium and J is called Coulomb integral. It is defined as J = $\left(1S_{(1)}1S_{(2)}\right) \middle| \frac{1}{r_{12}} \middle| \left(1S_{(1)}1S_{(2)}\right)$ and it measures the Coulombic repulsion between electrons.

Calculation of $E_{1S\,(i)}$:

In a two electron atom, the average potential experienced by an electron varies between

NOTE

$-\frac{1}{r_i}$ and $-\frac{2}{r_i}$ that is it depends on the effective nuclear charge experienced by the i^th^ electron in Helium atom. The best value of Z′ , the effective nuclear charge will be determined by the variation principle.

The wave function of 1S – orbital appropriate to this effective nuclear charge Z′ is

$$1S = \frac{(z')^{\frac{3}{2}} e^{-z' r}}{\sqrt{\pi}}$$

This orbital wave function is an eigen function of the

Hamiltonian operator $\left(-\frac{1}{2}\nabla^2 - \frac{z'}{r}\right)$.

with eigen value $\left(-\frac{z'^2}{2}\right)$

i.e. $$\left(-\frac{1}{2}\nabla^2 - \frac{z'}{r}\right)\frac{z'^{\frac{3}{2}} e^{-z' r}}{\sqrt{\pi}} = \left(-\frac{z'^2}{2}\right)\frac{z'^{\frac{3}{2}} e^{-z' r}}{\sqrt{\pi}}$$

$E_{1S}(i)$, energy of the i^th^ electron in the 1S orbital of helium atom.

i.e. $$E_{1S}(i) = \langle 1S(i)|H(i)|1S(i)\rangle$$

$$= \left\langle 1S(i)\left| -\frac{1}{2}\nabla_i^2 - \frac{2}{r_i}\right| 1S(i)\right\rangle$$

$$= \left\langle 1S(i)\left| -\frac{1}{2}\nabla_i^2 - \frac{z'}{r_i} + \frac{2}{r_i} \cdot \frac{z'}{r_i}\right| 1S(i)\right\rangle$$

$$= \left\langle 1S(i)\left| -\frac{1}{2}\nabla_i^2 - \frac{z'}{r_i}\right| 1S(i)\right\rangle - \left\langle 1S(i)\left| \frac{(2-z')}{r_i}\right| 1S(i)\right\rangle$$

NOTE

$$= \langle 1S\,(i) | -\frac{1}{2}\nabla_i^2 -$$

$$\frac{z'}{r_i} | 1S\,(i)\rangle - (2 - z')\langle 1S(i) | \frac{1}{r_i} | 1S\,(i)\rangle$$

$$= \frac{-z'^2}{2} - (2 - z')\,\langle 1S(i) | \frac{1}{r_i}\,| 1S(i)\rangle$$

$$E_{1S}(i) = \frac{-z'^2}{2} - (2 - z')$$

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \frac{z'^{3/2}}{\sqrt{\pi}} e^{-z' r_i} \frac{1}{r_i} \frac{z'^{3/2}}{\sqrt{\pi}} e^{-z' r_i} r_i^2\, dr\, Sin\theta d\theta d\phi$$

$$= \frac{-z'^2}{2} - (2 - z')\,\frac{z'^3}{\pi}\int_0^{\infty} e^{-2z' r_i} r_i\, dr_i \int_0^{\pi} Sin\theta d\theta \int_0^{2\pi} d\phi$$

$$E_{1S}(i) = \frac{-z'^2}{2} - (2 - z')\,\frac{z'^3}{\pi}\,.\,4\pi.\frac{L1}{(2z')^2}$$

$$E_{1S}(i) = \frac{-z'^2}{2} - (2 - z')\,z'$$

$E_{1S}(1) = E_{1S}(2)$.

Since electron (1) and (2) are equivalent.

$$E_{1s}(1,2) = 2\left(-\frac{z'^2}{2} - (2 - z')z' \right)$$

$$= -z'^2 - 4z' + 2z'^2$$

$$= z'^2 - 4z'$$

$$E = E_{1s}(1) + E_{1s}(1) + J \qquad J = \frac{5}{8}z'$$

$$E = z'^2 - 4z' + \frac{5}{8}z'$$

$$E = z'^2 - \frac{27}{8}z'$$

Minimizing the energy with respect to variable parameter $z' = \frac{\partial E}{\partial z'} = 0$

NOTE

$$\frac{\partial}{\partial z'}\left(z'^2 - \frac{27}{8}z'\right) = 0$$

$$2z' - \frac{27}{8} = 0$$

$$z' = \frac{27}{16} = 1.69$$

Substitution of this optimum value of z' in energy expression we get,

$$E = (1.69)^2 - \frac{27}{8} \times 1.69$$

$$= -2.8476au$$

$1au = 27.2eV$

E= -77.48eV

This is the approximate ground state energy of Helium atom. Experimental value is -2.904au (-79 eV). Thus variation principle accounts for 98% of the observed energy.

The effective nuclear charge experienced by an electron in Helium atom is 1.69 instead of the true charge 2. The difference in these two values 0.31 represents the screening of the nucleus by other electron and 0.31 is called the screening constant or shielding constant.

7.4 HMO Method

Huckel adopted an approximation method to estimate energy and wave function of the molecular orbital formed by the combination of π molecular orbital. The theory proposes the following approximation.

1. In a conjugated molecule the π electron does not interact with σ electron. The complete wave function ψ for the molecule is expressed as

$$\psi = \psi_\sigma, \psi_\pi$$

Where ψ_σ = complete wave function for σ electrons

ψ_π = complete wave function for π electrons.

The energy E of the molecule is expressed as,

$$E = E_\sigma + E_\pi$$

NOTE

2. Each HMO is considered as linear combination of 2P z atomic orbital

$$\psi_i = a_1p_1 + a_2p_2 + \ldots\ldots a_n p_n$$

$$\psi_i = \sum_{r=1}^{n} a_r p_r$$

Where ψ_i = i[th] HMO of the π electron system

p_r = $2P_z$ atomic orbital of the r[th] carbon

n = Total number of carbon atoms in the molecule

a_r = Coefficient of $2P_z$ orbital of r[th] carbon atom in the i[th] HMO

3. The energy of the i[th] HMO i.e. E_i is calculated by the formula,

$$E_i = \frac{\int \psi_i \hat{H} \psi_i d\tau}{\int \psi_i^2 d\tau}$$

Application of variation principle with 'n' number of carbon atoms gives 'n' number of secular equation of the following types.

$a_1(H_{11}-ES_{11}) + a_2(H_{12}-ES_{12}) + \ldots\ldots a_n(H_{1n}-ES_{1n}) = 0$

$a_1(H_{21}-ES_{21}) + a_2(H_{22}-ES_{22}) + \ldots\ldots a_n(H_{2n}-ES_{2n}) = 0$

.

.

$a_1(H_{n1}-ES_{n1}) + a_2(H_{n2}-ES_{n2}) + \ldots\ldots a_n(H_{nn}-ES_{nn}) = 0$

The corresponding n[th] order secular determinant is

NOTE

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & - & - & - & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & - & - & - & H_{2n}-ES_{2n} \\ - & - & - & - & - & - \\ - & - & - & - & - & - \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & - & - & - & H_{nn}-ES_{nn} \end{vmatrix} = 0$$

4. The columbic integrals Hp_i represents the energy of the electron in $2P_z$ orbital of i^{th} carbon atom

$$\text{i.e. } H_{ii} = \int p_i \, H \, p_i \, d\tau$$

where p_i is a wave function of $2P_z$ orbital of i^{th} carbon atom

All such integrals are equal and denoted by symbol α

$$H_{11} = H_{22} \ldots\ldots H_{ii}$$

$$H_{nn} = \alpha \text{ (say)}$$

5. The resonance integrals H_{rs} represent the energy of interaction between r^{th} carbon atom and s^{th} carbon atom.

$$\text{i.e. } H_{rs} = \int p_r \, \hat{H} \, p_s \, d\tau$$

where p_r is a wave function of $2P_z$ orbital of r^{th} carbon atom

p_s is a wave function of $2P_z$ orbital of s^{th} carbon atom

For non-bonded carbon atom $H_{rs} = 0$

For bonded carbon atom all such integrals are equal and denoted by symbol β

$$H_{12} = H_{23} \ldots\ldots H_{34} = \ldots = \beta$$

(say)

6. Integral of type S_{rr} is equal to one.

i.e. $$S_{rr} = \int p_r^{\,2} \, d\tau = 1$$

$$S_{11} = S_{22} \ldots\ldots S_{33} = \ldots\ldots = S_{nn} = 1$$

7. The overlap integrals S_{rs} are assumed to be zero though it is not actually zero. This assumption simplifies the calculation.

$$S_{rs} = \int p_r\, p_s\, d\tau$$

$$S_{12} = S_{23} = \ldots\ldots\ldots = 0$$

Hence the secular determinant for a linear conjugated polyene is of the following form.

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 \\ \beta & \alpha - E & \beta & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots \\ 0 & 0 & 0 & 0 & 0 \end{vmatrix}$$

Dividing each element by β and putting α-E/ β = x

Then

$$\begin{vmatrix} x & 1 & 0 & 0 & - & - & 0 \\ 1 & x & 1 & 0 & - & - & 0 \\ 0 & 1 & x & 1 & - & - & 0 \\ - & - & - & - & - & - & - \\ 0 & 0 & 0 & 1 & - & - & x \end{vmatrix}$$

The solution of the secular determinant is written as follows

$$X = -\, 2\cos\,(n\,\pi/N+1)$$

$$\alpha\text{-}E/\,\beta = -\, 2\cos\,(n\,\pi/N+1)$$

$$\alpha\text{-}E = -\, 2\,\beta\cos\,(n\,\pi/N+1)$$

$$\text{Energy } E_n = \alpha + 2\,\beta\cos\,(n\pi\ /N+1) \quad n = 1,2,3,\ldots\ldots N$$

n = order of energy level (or) order of molecular orbital.

N = Total number of carbon atoms in the molecule.

Thus, energy can be written as

$E_n = \alpha + 2\beta \cos (n\pi$

/N+1)

NOTE

7.5 Application to Butadiene

There are four $2p_z$ atomic orbital to be combined and four π electrons in the molecule. The HMO's are of the form, $\psi = a_1p_1 + a_2p_2 + a_3p_3 + a_4p_4$. Where a_1, a_2, a_3, a_4 are coefficients. There are four coefficients, so 4x4 determinants.

The secular determinant of the system is

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

$$x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

$$x \{[x(x^2-1)-1(x)\} -1\{[1(x^2-1)-1(0)\} = 0$$

$$x (x^3-x-x)-1(x^2-1) = 0$$

$$x^4- x^2 -x^2-x^2+1 = 0$$

$$x^4-3 x^2+1 = 0$$

Put $y = x^2$ $\quad y^2-3y+1 = 0$

$y = -(-3)\pm\sqrt{(-3)^2 - 4(1)(1)}\ / 2$ $\quad$ [$\because x = -b\pm\sqrt{b^2 - 4ac}\ /2a$]

$= 3\pm\sqrt{9-4}\ / 2$

$= 3\pm\sqrt{5}\ / 2$

$= 3\pm2.236/ 2$

$\therefore\ y = 0.382$ (or) $y = 2.618$

$y = x^2$

$x = \pm\sqrt{y}$ $\qquad$ $x = \pm\sqrt{y}$

$x = \pm\ \sqrt{0.382}$ $\qquad$ $x = \pm\sqrt{2.618}$

$x = +0.618$; $x = -0.618$ $\qquad$ $x = +1.618$; $x = -1.61$

Since α-E/β= x

$E = \alpha - \beta x$

$\therefore\ E_1 = \alpha + 1.618\ \beta$

$E_2 = \alpha + 0.618\ \beta$

$E_3 = \alpha - 0.618\ \beta$

and $\quad E_4 = \alpha - 1.618\ \beta$

Thus the total energy is, $E\ \pi = 2(\alpha + 1.618\ \beta) + 2(\alpha + 0.618\ \beta) - 4\alpha$

$= 4\alpha + 4.48\ \beta - 4\alpha$

$\therefore\quad {}_{\pi}$ Bond energy $= 4.48\beta$

Delocalization energy $= (4\alpha + 4.48\ \beta) - 2x2(\alpha + \beta)$

$= 4\alpha + 4.48\ \beta - 4\alpha - 4\ \beta$

$= 4.48\ \beta - 4\ \beta$

$= 0.48\ \beta$

Wave functions:

The wave functions corresponding to the energy levels E_1,E_2,E_3 and E_4 may be determined as follows.

The secular determinant for butadiene is

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix}$$

NOTE

The secular equations are obtained as follows

$$a_1x+a_2 = 0 \quad \rightarrow(1)$$

$$a_1+a_2x +a_3 = 0 \quad \rightarrow(2)$$

$$a_2+a_3x +a_4 = 0 \quad \rightarrow(3)$$

$$a_3+a_4x = 0 \quad \rightarrow(4)$$

For the energy level E_1 $x = -1.618$

Putting $x = -1.618$ in equation (1) we get,

$$a_1(-1.618) + a_2 = 0$$

$$\therefore a_2 = 1.618\, a_1$$

Substituting the value of a_2 and x in equation 2

$$a_1+1.618\, a_1(-1.618) +a_3 = 0$$

$$a_1-2.618a_1+a_3 = 0$$

$$a_3 = -1a_1+2.618a_1$$

$$a_3 =1.618a_1$$

Hence $a_2 = a_3$

Substituting the value of a_3 and x in equation 4, we get

$$1.618\, a_1+a_4(-1.618) = 0$$

$$\therefore a_1 = a_4$$

From the condition of normalization,

$$a_1^2+a_2^2 +a_3^2+a_4^2 = 1$$

$$\therefore \psi_1= a_1p_1+1.618\, a_1p_2+1.618a_1 p_3+a_4p_4$$

The wave function ψ_1 is normalized as follows

$$\int \psi^2 d\tau = 1 = \int (a_1 p_1 + 1.618 a_1 p_2 + 1.618 a_1 p_3 + a_1 p_4)^2 d\tau$$

$$[a_1^2 \int p_1^2 d\tau + (1.618a_1)^2 \int p_2^2 d\tau + (1.618a_1)^2 \int p_3^2 d\tau + a_1^2 \int p_4^2 d\tau = 1$$

$$\therefore a_1^2\,[1+2.618+2.618+1] = 1$$

$$7.236\,a_1^2 = 1$$

$$a_1 = 1/\sqrt{7.236}$$

$$\therefore a_1 = 0.372$$

$$a_2 = 1.618a_1$$

$$= 1.618(0.372)$$

$$a_2 = 0.602$$

$$a_3 = 1.618a_1 = 1.618(0.372)$$

$$a_3 = 0.602$$

Thus,

$$\psi_1 = 0.372p_1 + 0.602p_2 + 0.602p_3 + 0.372p_4$$

Similarly we can find for ψ_2, ψ_3 and ψ_4 by using the values x = -0.618, +0.618 and 1.618 respectively. The four HMO's of butadiene are thus found to be as follows:

$$\psi_1 = 0.372p_1 + 0.602p_2 + 0.602p_3 + 0.372p_4$$

$$\psi_2 = 0.602p_1 + 0.372p_2 - 0.372p_3 - 0.602p_4$$

$$\psi_3 = 0.602p_1 - 0.372p_2 - 0.372p_3 + 0.602p_4$$

$$\psi_4 = 0.372p_1 - 0.602p_2 + 0.602p_3 - 0.372p_4$$

7.6 Check Your Progress

1. Explain the HMO method.
2. Explain the HMO method and apply it to butadiene

7.7 Answers to Check Your Progress Questions

1. Huckel adopted an approximation method to estimate energy and wave function of the molecular orbital formed by the combination of π molecular orbital.

NOTE

2. There are four $2p_z$ atomic orbital to be combined and four π electrons in the molecule. The HMO's are of the form, $\psi = a_1p_1 + a_2p_2 + a_3p_3 + a_4p_4$. Where a_1, a_2, a_3, a_4 are coefficients. There are four coefficients, so 4x4 determinants. Using the HMO method, we derive, Bond energy = 4.48 β

7.8 Summary

The variation method to hydrogen atom gives,

$$E = \frac{1-2}{2} = -\frac{1}{2}\ au$$

This represents the exact value of energy and exact eigen function for hydrogen atom in its ground state. Any other wave function chosen will always lead to an energy greater than the lowest exact energy of the system.

7.9 Keywords

- **HMO**: Huckel Molecular Orbital.
- **Variation method**: For many problems, it is not practical to obtain a wave function by the exact solution of a wave equation that describes the system. It is still possible to perform many types of calculations, and one of the most useful techniques is that known as the *variation method*

7.10 Self-Assessment Questions and Exercises

1. Write down the steps involved in applying variation method.
2. State and explain variation theorem with proof and apply it to hydrogen atom.

7.11 Further readings

Quantum Chemistry, I.N. Levine, Allyn and Bacon, Boston, 1983.

Quantum Chemistry, R.K.Prasad, Wiley Eastern, New Delhi,1992.

BLOCK – III: *GROUP THEORY*

Unit-8: Assignment of point groups

Structure

8.0 Introduction

Group Theory is the mathematical applications of symmetry to an object to obtain knowledge of its properties. A point group describes all the symmetry operations that can be performed on a molecule that results in a conformation indistinguishable from the original. Point groups are used in Group Theory,the mathematical analysis of groups, to determine properties such as a molecule's molecular orbital. In this section we are going to focus on the Symmetry elements and symmetry operations, rules for forming a group, group multiplication table, group classification, Point groups and systematic assignment of point groups for molecules.

8.1 Objectives

After going through this unit, you will be able to:

- Understand about the Symmetry elements and symmetry operations.
- Understand the rules for forming a group, group multiplication table.
- Explain the concept of point groups and systematic assignment of point groups for molecules.

NOTE

8.2 Symmetry elements and symmetry operations

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SYMMETRY ELEMENT

A symmetry element is a geometrical entity such as a line or a plane or a point about which an operation of rotation or reflection or inversion is done.

SYMMETRY OPERATION

A symmetry operation is a movement of the molecule such that the resulting configuration of the molecule is indistinguishable from the original. The molecule is taken into an equivalent configuration or and identical configuration.

The symmetry elements and the corresponding symmetry operations are listed below:

Symmetry element	Symmetry operation
Proper axis of symmetry (C_n)	Rotation once or several times by an angle $\theta = (2\pi/n)$ about the axis.
Plane of symmetry (σ)	One or more reflections in the plane.
Improper axis of symmetry (S_n)	Rotation about the axis followed by reflection in a plane perpendicular to the rotation axis.
Centre of symmetry (i)	Inversion of all atoms through the centre of symmetry.
Identity element (E)	This operation leaves the molecule unchanged.

PROPER AXIS OF SYMMETRY (C_n)

This axis of symmetry can be explained by taking the example of triangular planar boron trichloride molecule. In boron trichloride molecule an axis of symmetry is located perpendicular to the plane containing all the atoms. This is known as the C_3 axis of symmetry. In general the symbol for proper axis of symmetry is C_n, where n is known as the order of the axis.

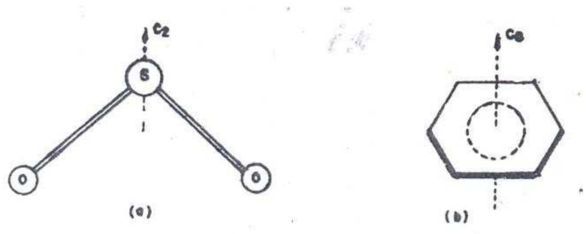
The order of the axis is given by the number of rotations by

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θ, to get the identical configuration. n is alternative given by the formula.

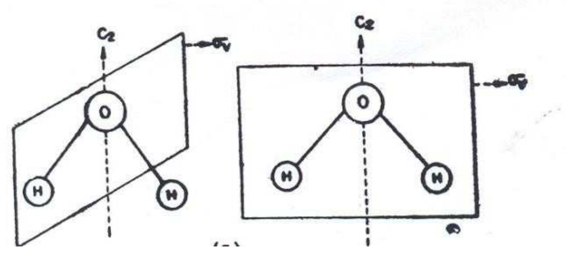
$$n = (2\pi/\theta)$$

where θ is the minimum angle of rotation to obtain the equivalent configuration.



PLANE OF SYMMETRY (σ)

The plane containing all the atoms is called as molecular plane. $[PtCl_4]^{2-}$ ion contains a molecular plane and four more reflection planes. Water has a reflection plane passing through the oxygen atom and another one containing all the atoms.



The reflections plane in water molecule

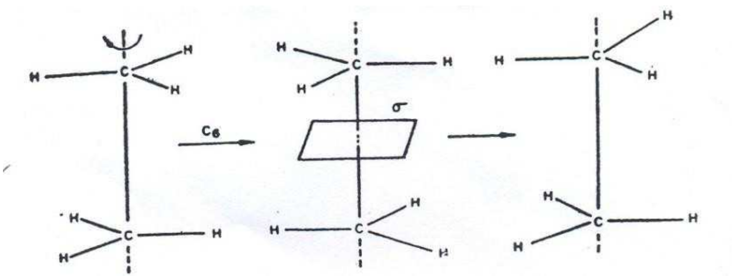
The reflection plane is of three types:-

i) A plane is referred to as horizontal plane (σ_h) if it is perpendicular to the principal axis.
ii) A reflection plane which contains the principal axis is called as vertical plane (σ_v).
iii) A vertical plane which bisects two perpendicular C_2 axes is called a dihedral plane (σ_d) e.g. allene.

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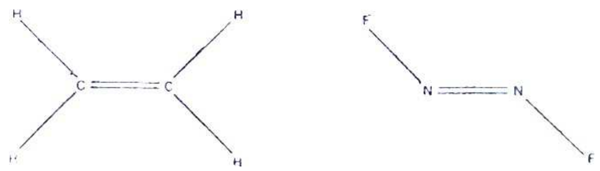
IMPROPER AXIS OF SYMMETRY (Sn)

It is the line about which a rotation by a specific angle followed by refletion in a plane perpendicular to the rotation axis is performed. E.g. S_6 axis in staggered form of ethane.



CENTRE OF SYMMETRY (i)

This is the point such that any line drawn through it meets the same atom at equal distances in opposite directions. All homonuclear diatomic molecules posses the centre of symmetry.



8.3 Rules for forming a group

The symmetry elements of a molecule must satisfy certain rules in order that they form a group. The rules are

1. The product of any two elements or square of each element must be an element of that group.
2. In each group, there is one element which commutes with every other element and leaves it unchanged. In general the identity element does so.
3. The associative law of multiplication hold good.
4. Each element has an inverse or reciprocal which is also element of that group.

If the element is A and its inverse is A^{-1}

Then, $A\,A^{-1} \equiv E$

For e.g. consider the set of numbers

{1/4, 1/2, 1, 2, 4, 8, 16}

By rule (1)

2 x 4 = 8

$2^2 = 4$

$4^2 = 16$

By rule (2)

$A^{\wedge}B^{\wedge}=B^{\wedge}A^{\wedge}$

1x2 = 2x1 = 2

1x4 = 4x1 = 4

By rule (3)

A (BC) = (AB) C

2(4x8) = (2x4)8

By rule (4)

$A\ A^{-1}$

½ x 2 =1

¼x4=1

8.4 Group multiplication table

It consists of rows and columns. Each is represented by a group element. For multiplication we can use the following method. i.e. Column element x Row element.

For constructing a group, rearrangement theorem must be known. It states,

“ In each column or a row a particular elements occur only one”.

For example,

Consider a group of order 2. This group consists of two elements only. Let the elements be E and A. The first step leads to the following table.

G_2	E	A
E	E	A
A	A	X

NOTE

According to rearrangement theorem 'X' should be 'E' only and cannot be 'A'. ∴the group multiplication table of G_2 is

Example -2

E	C_2	σ_v	σ_v'
C_2	E	σ_v'	σ_v
σ_v	σ_v'	E	C_2
σ_v'	σ_v	C_2	E

The following features of the multiplication table carry significance:

1) E combining with any operation X gives X as the result since E does "nothing" i.e., EX=XE =X.
2) C_2 performed on any object, interchanges both left and right and front and back.
3) σ_v interchanges only left and right while σ_v', interchanges only front and back.
Thus $\sigma_v \sigma_v' = \sigma_v' \sigma_v$ is the same as front-back +left, -right interchange

i.e. $C_2 C_2 \sigma_v = \sigma_v' \sigma_v \sigma_v = \sigma_v' E = \sigma_v'$ and similarly $C_2 \sigma_v' = \sigma_v$

8.5 Group classification

FINITE GROUP

A group that contains definite number of symmetry elements is called the finite group. For example, water molecule has 4 elements of symmetry and Ammonia molecule has 6 elements of symmetry. Therefore they belong to the finite group.

INFINITE GROUP

A group that contains infinite number of symmetry elements these are called as infinite group.

For example: linear molecules H_2 (H-H), Br_2 (B_r-B_r), HCl and CO_2 can be rotated along the molecular axis to any degree. Therefore they have infinite axes of symmetry. Such molecules belongs to infinite group.

ABELIAN GROUP

Abelian group is a group in which each element commutes

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with every other elements.

For eg:- In water molecule, each element commutes with every other element and therefore water molecule belongs to abelian group. Such a situation dos not arise in NH_3 molecule and hence it is non-abelian.

CYCLIC GROUP

A group in which one element generates all the other elements of the group is known as cyclic group.

For e.g. the elements of symmetry that are present in H_2O_2 are E and C_2. The element C_2 generates the other element E since $C_2^2 \equiv E$.

SUB GROUP

A sub group is the smaller group of a main group in which the elements of symmetry must satisfy the requirements for forming a group.

The order of a subgroup is given by 'g'. The order of a maingroup is the integral multiple of the order of the subgroup.

$$h = g \times n$$

Where 'n' is the integer.

In water molecule, there are four subgroups. They are

(E) (E, C_2) (E, σ_v) and (E, $\sigma_{v'}$)

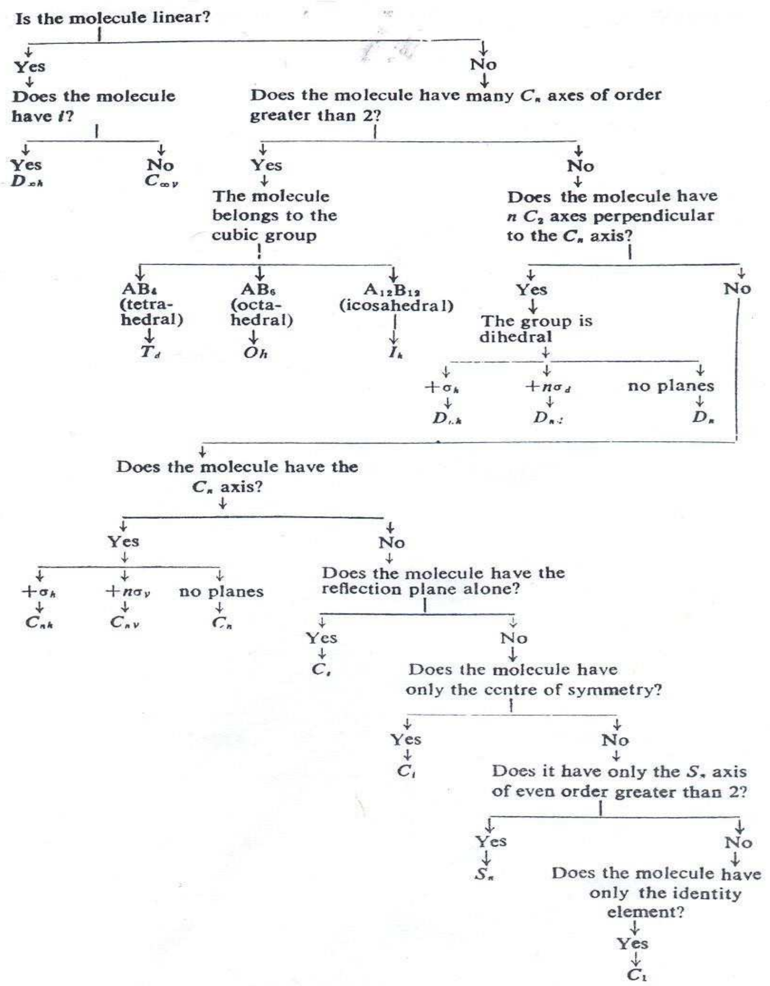
In general, the identity element in any group will form one of the subgroup.

8.6 Point groups and systematic assignment of point groups for molecules

POINT GROUPS

Depending upon the symmetry elements molecules are classified in to different groups. Molecular groups are called point groups. Because the symmetry elements intersect at a point and this point does not move during symmetry operations. Molecules are classified into different point groups based on certain combinations of symmetry operatins. The system of notation used for point group is known as schoenflies system. In this case symbols like C_{nv} , D_{nh} , O_h and T_d are used. In order to identify the point group, the following flow chart will be helpful.

NOTE



8.7 Check Your Progress

1. Distinguish symmetry elements and symmetry operations?
2. Explain Centre of symmetry?
3. Define Cyclic group?
4. Define Point group?

NOTES

8.8 Answers To Check Your Progress Questions

1.

Symmetry element	Symmetry operation
Proper axis of symmetry (C_n)	Rotation once or several times by an angle $\theta = (2\pi/n)$ about the axis.
Plane of symmetry (σ)	One or more reflections in the plane.
Improper axis of symmetry (S_n)	Rotation about the axis followed by reflection in a plane perpendicular to the rotation axis.
Centre of symmetry (i)	Inversion of all atoms through the centre of symmetry.
Identity element (E)	This operation leaves the molecule unchanged.

2. This is the point such that any line drawn through it meets the same atom at equal distances in opposite directions. All homonuclear diatomic molecules posses the centre of symmetry.

3. A group in which one element generates all the other elements of the group is known as cyclic group. e.g. the elements of symmetry that are present in H_2O_2 are E and C_2. The element C_2 generates the other element E since $C_2^2 \equiv$ E.

4. Depending upon the symmetry elements molecules are classified in to different groups. Molecular groups are called point groups.

8.9 Summary

- A point group describes all the symmetry operations that can be performed on a molecule that results in a indistinguishable from the original.
- The different types of groups and their definition are symmerized.
- Symmety elements and their operation such as Proper axis of symmetry (C_n), Plane of symmetry (σ), Improper axis of symmetry (S_n) and Centre of symmetry (i) are clearly explained.

8.10 Keywords

Point group: point group describes all the symmetry operations that can be performed on a molecule that results in a conformation indistinguishable from the original.

Group classification: A subset of a group that is closed under the group operation and in which every element has an inverse in the subset.

Group multiplication table: Every row contains each element exactly once and every column contains each element exactly one.

NOTE

8.11 Self-assessment questions and exercises

1. Explain in detail about the rules for forming a group
2. Discuss in detail about symmetry group and operations
3. Dicuss the point group
4. Explain Group classification

8.12 Further readings

3. **Chemical Application of Group Theory**, F.A. Cotton, John Wiley and Sons Inc. New York,1971.

4. **Group theory and its applications to Chemistry**, K.V. Raman, Tata McGraw-Hill Publishing Company,1990.

Unit- 9 Matrix representation theory

Structure

9.0 Introduction

The symmetry operations in a group may be represented by a set of transformation matrices, one for each symmetry element g. Each individual matrix is called a **representative** of the corresponding symmetry operation, and the complete set of matrices is called a **matrix representation** of the group**.** In this context, we discuss in detail about matrix representation theory,matrix multiplication, inverse of a matrix, matrixdiagonalization and matrix representation for symmetry operations

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9.1 Objectives

After going through this unit, you will be able to:

- Understand the concept Matrix representation theory
- Explain the Matrix multiplication and Inverse of matrix.
- Understand the Matrix diagonalization and Matrix representation for symmetry operations.

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9.2 Matrix representation theory

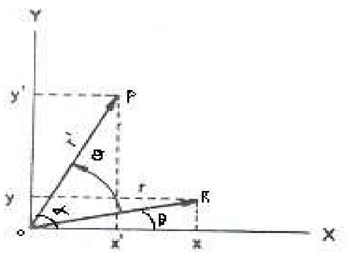
During a symmetry operation, a set of coordinates of an atom in a molecule is transformed into a new set of coordinates. These two sets are related to one another in the form of a set of equations. This set of equation can be formulated in the form of a matrix. Each symmetry operation is represented by a matrix. Matrix representation of the symmetry operation is useful in the study of structural problems.

9.3 Matrix representation for symmetry operations

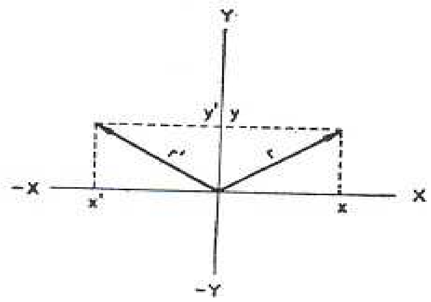
The matrix representation for each kind of symmetry operation can be obtained as follows.

Cn OPERATION

Consider the figure shown,



(a)



The position of an atom in a molecule is represented by the vector OP whose magnitude is 'r'. Point 'P' corresponds to the coordinates x,y,z. If the molecule is

Rotated in the clockways direction through an angle θ the atom changes its position from the point 'P' to the point 'R'. point 'R' has a new set of coordinates namely $x_2y_2z_2$.

Consider the ΔPOQ, it follows from the knowledge of trigonometry that,

$$x_1 = OQ = r \text{ Cos } \alpha$$

$$y_1 = PQ = r \sin \alpha$$

Consider the ΔROS,

Again,

$$x_2 = OS = r \cos \beta = r \cos (\alpha - \theta)$$

$$y_2 = RS = r \sin \beta = r \sin (\alpha - \theta)$$

$z_2 = z_1$ (since the rotation is carried out about the z-axis).

NOTES

$\therefore x_2 = r \cos \alpha \cos \theta + r \sin \alpha \cos \theta = x_1 \cos \theta + y_1 \sin \theta + 0$

$y_2 = r \sin \alpha \cos \theta - r \cos \alpha \sin \theta = y_1 \cos \theta + x_1 \sin \theta + 0$

$= 0 + 0 + z_1.$

$Z_2 = z_1$

$\cos(\alpha \pm \beta) = \cos \alpha \cos\beta \pm \sin \alpha \sin \beta$

$\sin(\alpha \pm \beta) = \sin \alpha \cos\beta \pm \cos \alpha \sin \beta$

This set of equations can be formulated in the form of a matrix.

$$\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix}$$

Therefore the matrix representation for C_n axis is given as,

$$C_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

If the rotation is carried out in the anticlock direction, the matrix will be,

$$C_n = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

For e.g. the matrix representation for a C_2 axis is given by

$$C_2 = \begin{bmatrix} \cos 180 & \sin 180 & 0 \\ -\sin 180 & \cos 180 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

NOTE

$$C_3 = \begin{bmatrix} \cos 120 & \sin 120 & 0 \\ -\sin 120 & \cos 120 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

For an identity operation, the new set of coordinates will be the same as that of the original.

cos (90+θ) = sin θ

cos (270+θ) = sin θ

sin (90+θ) = cos θ

sin (270+θ) = cos θ

Therefore,

$x_2 = x_1 + 0 + 0$

$y_2 = 0 + y_1 + 0$

$z_2 = 0 + 0 + z_2$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix}$$

∴ The matrix representation for the identity operation is given as,

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

INVERSION OPERATION

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$x_2 = -x_1 + 0 + 0$

$y_2 = 0 - y_2 + 0$

$z_2 = 0 + 0 - z_2$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix}$$

$\therefore$ The matrix representation for the identity operation

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

REFLECTION OPERATION

During a reflection operation, the coordinates corresponding to the reflection plane do not change the sign while that of the other coordinates change their sign. Therefore the matrices corresponding to the reflection operation is given below,

$$o_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$o_{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

NOTE

S_n OPERATION

S_n operation involves rotation of the molecule about an axis through an angle followed by reflection in a plane perpendicular to the axis. ∴ the matrix for a S_n operation is obtained by multiplying the matrices corresponding to C_n and σ_{xy} provided z-axis is taken as the rotational axis.

$$S_n = C^{z} \sigma^{xy}$$

$$S_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$S_3^5 \equiv C_{3\sigma}^{5} \equiv C_3^{2}\sigma$$

9.4 Inverse of matrix

A square matrix B is called the inverse of A if

$$AB = BA = 1$$

Where I is the unit matrix. Inverse does not exist if the matrix is singular. The inverse of the matrix A can be obtained by using the following rules:

1. Compute the determinant of the matrix A.
2. Interchange the elements a_{11} and a_{22}.
3. Change the signs of a_{12} and a_{21}.
4. Divide each element of the matrix thus formed by the determinant of A.

$$A = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix}$$

NOTES

The resulting matrix is the inverse of A and is represented as A^{-1}. The inverse of the matrix B

$$B = \begin{bmatrix} 3 & -2 \\ 1 & 4 \end{bmatrix}$$

is obtained as follows. The determinant of the matrix B is equal to 14. Interchange of the elements 3 and 4 leads to the matrix.

$$\begin{bmatrix} 4 & -2 \\ 1 & 3 \end{bmatrix}$$

When the signs of -2 and 1 are changed, the following matrix results:

$$\begin{bmatrix} 4 & 2 \\ -1 & 3 \end{bmatrix}$$

Each element of this matrix is divided by 14 to obtain the inverse of B.B^{-1} thus obtained is given below:

$$B^{-1} = (1/4) \times \begin{bmatrix} 4 & 2 \\ -1 & 3 \end{bmatrix}$$

9.5 Diagonalisation of a matrix

The process of reducing a matrix to the diagonal matrix is referred to as diagonalisatoin. Let A be the square matrix of order n. P is the similarity transformation matrix which reduces A to the diagonal matrix D according to the equation.

$$p^{-1} AP = D$$

NOTE

Let us consider the matrix A

$$A = \begin{bmatrix} -7 & 6 \\ -18 & 14 \end{bmatrix}$$

The similarity transformation matrix P

$$P = \begin{bmatrix} 2 & 1 \\ 3 & 2 \end{bmatrix}$$

And its inverse P^{-1}

$$P^{-1} = \begin{bmatrix} 2 & -1 \\ -3 & 2 \end{bmatrix}$$

can be used to reduce A to the diagonal matrix according to the equation

$$P^{-1}AP = \begin{bmatrix} 2 & -1 \\ -3 & 2 \end{bmatrix} \times \begin{bmatrix} -7 & 6 \\ -18 & 14 \end{bmatrix} \times \begin{bmatrix} 2 & 1 \\ 3 & 2 \end{bmatrix}$$

$$= \begin{bmatrix} 2 & 0 \\ 0 & 5 \end{bmatrix}$$

NOTES

9.6 Matrix representation for symmetry operations

Using carthesian coordinates (x,y,z) or some **position vector**, we are able to define an initial position of a point or an atom.

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

The initial vector is submitted to a symmetry operation and thereby transformed into some resulting vector defined by the coordinates x', y' and z'. In an algebraic context, this transformation is expressed a matrix which processes the initial position vector. We write

*final vector = Matrix * initial vector.*

The most primitive symmetry operation is the identity and yields a final vector identical to the initial vector. It is the **unity matrix** or **identity matrix** which leaves all coordiates unaffected.

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

If we want to perform a **reflection** on the xy-plane (analogous to a horizontal plane σ_h), coordinate z changes the sign.

$$\sigma_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\begin{pmatrix} x \\ y \\ -z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

NOTE

The matrices which are applied for performing a reflection on the yz-plane and xz-plane are the matrices σ_x and σ_y respectively.

$$\sigma_x = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

The **inversion *i*** relates the coordinates (x,y,z) with (-x,-y,-z) and is connected with the following matrix:

$$i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Obviously, a twofold application of the inversion matrix yields the coordinates of the initial point (x,y,z) which is reflected by ***E* = *i*i***.

$$i \cdot i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = E$$

The matrix for a rotation about axis z by an arbitrary angle Θ is derived easily if we imagine two two-dimensional coordinate planes with identical origin but an angular difference of Θ between the axes. In our context of symmetry, we just need to deal with the discrete values of Θ = 2π/n for the angle of rotation.

$$C_n = \begin{pmatrix} \cos 2\pi/n & \sin 2\pi/n & 0 \\ -\sin 2\pi/n & \cos 2\pi/n & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The matrices for the symmetry operations $C_2(z)$, $C_3(z)$, $C_4(z)$, $C_5(z)$ and $C_6(z)$ are obtained easily. The matrices for C_n^m as symmetry operation are calculated by an n-fold multiplication of matrix C_n. The symmetry operation C_2 around axis x (x→x,y→-y, z→-z) and around axis y are (x→-x, y→y, z→-z):

NOTES

$$C_2(x) = \begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

$$C_2(y) = \begin{vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

As we know rotatory-reflection to be a combination of rotation and reflection, a matrix representation for this operation is easily to be derived.For instance, to obtain the matrix for rotatory reflection $S_n(z)$ we multiply the matrices for the fundamental operations &sigma$_z$ and C_n.

$$S_n(z) = \sigma_z C_n = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix} \begin{pmatrix} \cos 2\pi/n & \sin 2\pi/n & 0 \\ -\sin 2\pi/n & \cos 2\pi/n & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \cos 2\pi/n & \sin 2\pi/n & 0 \\ -\sin 2\pi/n & \cos 2\pi/n & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

9.7 Check Your Progress

1.What is matrix representation?
2.Givethe rules of Inverse of matrix?
3.what is the equation of S_n OPERATION

4.what are the types of symmetry operations in matrix representation?

9.8 Answers to check your progress questions

1. The symmetry operations in a group may be represented by a set of transformation matrices, one for each symmetry element g. Each individual matrix is called a representative of the corresponding symmetry operation, and the complete set of matrices is called a **matrix representation** of the group.

2.

- Compute the determinant of the matrix A.
- Interchange the elements a_{11} and a_{22}.
- Change the signs of a_{12} and a_{21}.
- Divide each element of the matrix thus formed by the determinant of A.

NOTE

3.

$$S_n = C^{z}\,\sigma^{xy}$$

$$S_n = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$S_3^5 \equiv C_{3\sigma}^{\ 5} \equiv C_3^2\sigma$$

4.

- C_n operation
- S_n operation
- Inverse operation
- Reverse operation

9.9 Summary

- A matrix representation theory describes all the symmetry operations that can be performed on a mathematical experision
- The process of reducing a matrix to the diagonal matrix is referred to as diagonalisatoin.
- Matrix representation of the symmetry operation is useful in the study of structural problems.

9.10 Keywords

Matrix representation-A set matrix of symmetry operations.
Inverse of matrix -AB = BA = 1

Operations - C_n, S_n, Inverse Reverse operation

9.11 Self-assessment questions and exercises

1. Explain in detail about Matrix representation theory and matrix multiplication
2. Give a brief review Inverse of a matrix
3. Explain matrix representation for symmetry operations

9.12 Further readings

1. **Chemical Application of Group Theory**, F.A. Cotton, John Wiley and Sons Inc. New York,1971.
2. **Group theory and its applications to Chemistry**, K.V. Raman, Tata McGraw-Hill Publishing Company,1990.

NOTES

UNIT- 10 Character table

NOTE

Structure

10.0 Introduction

Representation is a set of matrices which represent the operations of a point group. It can be classified in to two types, which are reducible representations and irreducible representations**.** A character table is a 2 dimensional chart associated with a point group that contains the irreducible representations of each point group along with their corresponding matrix characters. It also contains the Mulliken symbols used to describe the dimensions of the irreducible representations, and the functions for symmetry symbols for the Cartesian coordinates as well as rotations about the Cartesian coordinates. In this context, we discuss in detail about reducible and irreducible representations,Character table of C2v and C3v point groups,the great orthogonality theorem and character and direct product representation.

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10.1 Objectives

After going through this unit, you will be able to:

- Explain about the reducible and irreducible representations
- Understand about the character table of C2v and C3v point groups
- Understand the concept of the great orthogonality theorem and character
- Learn about the direct product representation.

10.2 Reducible and irreducible representations

REDUCIBLE REPRESENTATION

Reducible representation and its reduction can be undearstood by carrying out a similarity transformation.

Let A,B,C,D and P be the similarity transformation matrix in this group.By similarity transformation the matrices A,B,C,D and P are changed into A′,B′,C′,D′ and P′ as

$$P^{-1} AP = A'$$

$$P^{-1} BP = B'$$

$$P^{-1} CP = C'$$

$$P^{-1} DP = D'$$

$$P^{-1} PP = P' = P$$

If the resulting matrices can be blocked into smaller matrices, then the representation Γ is called a reducible representation. For e.g. A′ can be blocked into a_1', a_2', a_3', a_4',……… a_6', as sub-matrices as

$$A^1 = \begin{bmatrix} a_1^1 & 0 & 0 & 0 & 0 & 0 \\ 0 & a_2^1 & 0 & 0 & 0 & 0 \\ 0 & 0 & a_3^1 & 0 & 0 & 0 \\ 0 & 0 & 0 & a_4^1 & 0 & 0 \\ 0 & 0 & 0 & 0 & a_5^1 & 0 \\ 0 & 0 & 0 & 0 & 0 & a_6^1 \end{bmatrix}$$

A reducible representation result when the various symmetry operations are performed on all the sigma-bonds of a molecule for e.g. In BF_3 molecule (D_3h point group) the 12 symmetry operations of this group are divided into 6 classes as

NOTE

(E) (C_3^1, C_3^2), $(3C_2^1)$,$(3\sigma_v)$,(S_3^1, S_3^5) and (σ_h).

The three sigma-bonds in BF_3 are considered as vectors r_1, r_2 and r_3. By a symmetry operation R, the vectors r_1, r_2 and r_3 r_1, r_2 and r3 are changed into r_1' ,r_2' and r_3' according to matrix equation.

$$\begin{bmatrix} r_1^1 \\ r_2^1 \\ r_3^1 \end{bmatrix} = [R] \begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix} \rightarrow (a)$$

Where [R] is the matrix for the operation R. The equations relating r_1' , r_2' and r3′ and r_1, r_2 and r_3 are

$$r_1^1 = 1r_1 + 0r_2 + 0r_3$$

$$r_2^1 = 0r_1 + 1r_2 + 0r_3$$

$$r_3^1 = 0r_1 + 0r_2 + 1r_3$$

In matrix form the above equation becomes

$$\begin{bmatrix} r_1^1 \\ r_2^1 \\ r_3^1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix} \rightarrow (b)$$

From equations (a) and (b) we get

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

As the matrix for identity operation.

For C_3^1 operation the resulting vectors r_1' , r_2' and r_3' are related to r_1, r_2 and r_3 by the equation.

$$r_1^1 = 0r_1 + 1r_2 + 0r_3$$

$$r_2^1 = 0r_1 + 0r_2 + 1r_3$$

$$r_3^1 = 1r_1 + 0r_2 + 0r_3$$

These equations can be represented in the matrix form as

$$\begin{bmatrix} r_1^1 \\ r_2^1 \\ r_3^1 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \times \begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix} \rightarrow (c)$$

From (a) and (c), we get,

$$c_3^1 = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}$$

Similarly we get reducible representation for

$$\underset{\sigma_v}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}} \underset{\sigma_h}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}} \underset{S_3^1}{\begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}} \underset{C_2^1}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}}$$

The characters of the matrices can be found by using the rule "The character of the matrix for a symmetry operation is equal to the number of unshifted vectors by the operation".

The number of vectors unshifted by the identity operation is three.

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The character for this matrix is also 3.

By using the rule the characters for the different matrices of operations of BF_3 are obtained.

NOTE

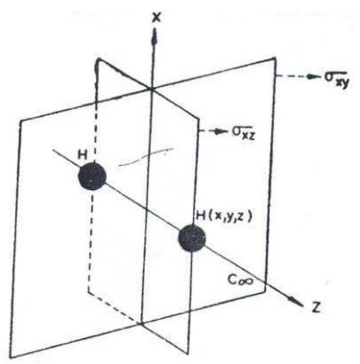
Symmetry operations	E	C_3^1	C_2^1	σ_h	σ_v	S_3^1
Character of the matrix	3	0	1	3	1	0

IRREDUCIBLE REPRESENTATION

If it is not possible to find a similarity transformation matrix which will reduce the matrices of representation Γ then the representation is said to be irreducible. All one-dimensional representations are always irreducible.

Example:

Considering the matrices of transformation for the Z-coordinate of a hydrogen atom in hydrogen molecule, which result by the symmetry operations of $D_\infty h$ group. The operations of $D_\infty h$ group are E, C_∞, σ_v, C_2 , σ_h, S_∞ and i. From the figure the Z-coordinate is unaffected by E, C_∞ and σ_v operations.



The C_∞ axis, vertical plane and horizontal plane in H_2 molecule

The equations and matrices for the transformation of Z-coordinate of hydrogen atom by these operations are

E.Z = 1Z

E matrix = [1]

C_∞ . Z = 1Z C_∞.

matrix = [1]

σ_v.Z = 1Z

σ_v.matrix = [1]

All the other operations of this group change the coordinate Z of hydrogen atom into –Z, we get

$$c_2 .z = -1z$$
$$s_\infty .z = -1z$$
$$\sigma_h .z = -1z$$
$$i.z = -1z$$

C_2 matrix = [-1]

s_∞ matrix = [-1]

σ_h matrix = [-1]

i matrix = [+1]

The matrix representation thus obtained for the z-coordinate of the hydrogen atom in the hydrogen molecule is given below.

	E	C_∞	σ_v	C_2	S_∞	σ_h	i
Γ	[1]	[1]	[1]	[-1]	[-1]	[-1]	[-1]

This representation Γ is irreducible since it is one-dimensional.

NOTE

Reducible representations and irreducible representation play an important role in obtaining solutions to problems of hybridization, molecular vibration, delocalization energies of Π electron system and so on. In all this applications the first step involves point group determination and formation of the reducible representations of the group. Every point group consists of a certain number of irreducible representations.

The characters of matrices in the different irreducible representations of a point group can be listed in a table known as character table. The character table for a group can be constructed with the knowledge of properties of irreducible representation. The properties of irreducible representation can be obtained from the great orthogonality theorem.

PROPERTIES OF IRREDUCIBLE REPRESENTATIONS

A knowledge of the properties of irreducible representations is essential to construct the character table of a point group.

Let us consider a point group consisting of h symmetry operations. These operations are divided into K classes. The irreducible representations are denoted as Γ_1, Γ_2.....................Γ_k. l_1, l_2……..l_k are dimensions of these representations. The orthogonalilty theorem is used to obtain the following rules for the irreducible representations.

1. The number of irreducible representations in a group is equal to the number of classes in the group.
2. The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group.

$$\sum_{i=1}^{K} l_i^2 = h$$

NOTES

$$l_1^2 + l_2^2 + l_3^2 \cdots\cdots = h$$

In a matrix of order l there are square elements thus each irreducible representation Γ_i will provide $l_i^2 = h$ dimensional vector. The basic theorem requires this set of $l_1^2 + l_2^2 + l_3^2$ ……… vectors to be mutually orthogonal. Since there can be more than h dimensional, h orthogonal vectors the sum of $l_1^2 + l_2^2 + l_3^2$ ……… may not exceed h.

3. The sum of the squares of the characters of identity operation in the irreducible representation is equal to the order of the group h.

$$\sum_{i=1}^{k} (x_i(E))^2 = h$$

$$\sum_R [\chi_i(R)]^2 = h$$

4. The vectors whose components are the characters of two different irreducible representation are orthogonal.

$$\sum_R \chi_i(R)\chi_j(R) = 0 \quad ; \text{Where } i \neq j$$

5. In a given representation the characters of all matrices belonging to operation in the same class are identical.

Symbols used for representing irreducible representation:

1. Bethe's method is used to label irreducible representation such as Γ_1, Γ_2, Γ_3.
2. Mullikan's method is based on symmetry of irreducible representation.
3. Symbol A or B represents one dimensional representation. E represents two dimensional representations and Γ represents three dimensional representation.
4. If Γ= +1 with respect to principle axis, the symbol A is used. If Γ = -1 the symbol B is used. If there are several irreducible representation subscript 1, 2, 3 etc are used.
   Example:

   A_1, A_2, A_3………………..

   B_1, B_2, B_3…………………

   E_1, E_2, E_3…………………

   Γ_1, Γ_2, Γ_3…………………

NOTE

If there is only one representation the subscript one is not necessary.

5. If the operation is inversion and Γ = +1 the subscript g is used (g=gerade). If the operation is inversion and Γ = -1 the subscript v is used (ungerade).
6. If Γ = 1 for all the symmetric operation of a point group A_1 or Ag is used which is called totally symmetric irreducible representation.
7. Single prime denotes that the irreducible representation is symmetric with respect to σ_h.
8. Double prime denotes, that the irreducible representation is antisymmetric with respect to σ_h.

10.3 Character table of C2v and C3v point groups

CHARACTER TABLE

The characters of matrices in the different irreducible representations of a point group can be listed in a table known as character table.

CONSTRUCTION OF CHARACTER TABLE FOR C_2V POINT GROUP

C_2V point group consists of 4 elements such as E, C_2, σ_{vxz} and σ_{vyz}, each is in a separate class. Hence, as per rule

(1) i.e. the number of irreducible representations of a group is equal to the number of classes of the group.

C_2V	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
Γ_1				
Γ_2				
Γ_3				
Γ_4				

NOTES

There are 4 irreducible representations of this group but it is also required as per rule.

(2) "The sum of the squares of the dimensions of the irreducible representation of a group is equal to the order of the group h". Thus we are looking for a set of 4 '+ ve', integers , l_1, l_2, l_3 and l_4 which satisfy the relation, $l_1^2 + l_2^2 + l_3^2 + l_4^2 = h$. clearly the only solution is $l_1 = l_2 = l_3 = l_4 = 1$. Thus the group C_2V have 4 one dimensional irreducible representations.

On the basis of the vector properties of the representations and the rules derived above, one suitable vector in four space which has a component of one corresponding to Γ_1 will obviously be 1,1,1,1 for

$$\sum_R [\chi_i(R)]^2 = h$$

$$1^2 + 1^2 + 1^2 + 1^2 = 4$$

NOTE

C_2V	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
Γ_1	1			
Γ_2	1			
Γ_3	1			
Γ_4	1			

Thus satisfying rule

(3) i.e. the sum of the squares of their characters in any irreducible representation equals h.

C_2V	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
Γ_1	1	1	1	1
Γ_2	1			
Γ_3	1			
Γ_4	1			

Now all other representations will have to be such that $\Sigma[X_i(R)]^2$ =h=4 which can be true only if each $X_i(R)= \pm 1$. Moreover in order for each of the other representations to be orthogonal to Γ_1. According to the rule

(4) i.e. the vectors whose components are the characters of two different irreducible representation are orthogonal.

$$\text{i.e. } \sum_R X_i(R)\, X_i\,(R) = 0 \quad \text{when } i \neq j.$$

There will have to be 2 "+1'S" and 2"-1'S".

(1) (1)+ (1) (-1)+ (1) (-1) +(1) (1) = 0

Therefore we can write the other irreducible representation as follows.

C_2V	E	C_2	$\sigma_{V(XZ)}$	$\sigma_{V(yZ)}$
Γ_1	1	1	1	1
Γ_2	1	-1	-1	1
Γ_3	1	-1	1	-1
Γ_4	1	1	-1	-1

CONSTRUCTION OF CHARACTER TABLE FOR C_3V POINT GROUP

C_3V point group consists of 6 symmetry elements. E, C_3^1, C_3^2, σ_V, σ_V' and σ_V''. It can be listed by classes as E $2C_3$, $3\sigma_V$. Rule (1) is the number of irreducible representation = number of classes.

C_3V	E	$2C_3$	$3\sigma_V$
Γ_1			
Γ_2			
Γ_3			

We therefore known that there are 3 irreducible representations, by rule (1), if we denote the dimensions by l_1, l_2 and l_3 we have $l_1^2 + l_2^2 + l_3^2 = h = (6)$. The only values of the l_i which will satisfy this requirement are 1,1and 2.

C_3V	E	$2C_3$	$3\sigma_V$
Γ_1	1		
Γ_2	1		
Γ_3			

Thus as by rule (2), the sum of the squares of the dimensions of the irreducible representation of a group is equal to h.

$$1^2 + 1^2 + 2^2 = 1+1+4 = 6$$

Always in any group there will be a one dimensional representation whose character is equal to +ve one. Therefore one dimensional irreducible representation in C_3V point group is.

NOTE

C_3V	E	$2C_3$	$3\sigma_V$
Γ_1	1	1	1
Γ_2	1		
Γ_3	2		

Thus by rule (3)

The sum of the squares of the characters of identity operation in the irreducible representation is equal to the order of the group h.

$\Sigma[X_i(R)]^2 = h = -1(1)^2 + 2(1)^2 + 3(1)^2 = 6$

As per rule (4), the vectors whose components are the characters of two different irreducible representations are orthogonal.

We now look for a 2nd vector in space whose components are equal to + or -1which is orthogonal to Γ_1 . The components of such a vector must consists of 3'+1'S' and 3'-1'S'. Since X(E) must always be '+ve' and since all elements in the same class must have representations with the same character, the only possibility here is

C_3V	E	$2C_3$	$3\sigma_V$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2		

Now our 3rd representation will be of two dimension i.e.$X_3(E) = 2$. In order to find out the values of $X_3(C_3)$ and $X_3(\sigma_V)$, we make use of orthogonality relationship.

$$\sum_R \chi_1(R)\chi_3(R) = 0$$

$$\sum_R \chi_1(R)\chi_3(R) = (1)(1)(2) + (2)(1)(\chi_3 C_3) + (3)(1)(\chi_3\sigma_V) = 0$$

$$= 2 + 2\chi_3 C_3 + 3\chi_3\sigma_V = 0$$

$$\sum_R \chi_2(R)\chi_3(R) = (1)(1)(2) + (2)(1)(\chi_3 C_3) + (3)(-1)(\chi_3\sigma_V) = 0$$

$$= 2 + 2\chi_3 C_3 - 3\chi_3\sigma_V = 0$$

$$2\chi_3 C_3 + 3\chi_3\sigma_V = -2 \rightarrow (1)$$

$$2\chi_3 C_3 - 3\chi_3\sigma_V = -2 \rightarrow (2)$$

$$4\chi_3 C_3 + \; = -4$$

$$\chi_3 C_3 = \frac{-4}{-4} = -1$$

Substitute $\chi_3 C_3 = -1$ in equation (1)

$$2(-1) + 3\chi_3\sigma_v = -2$$

$$-2 + 3\chi_3\sigma_v = -2$$

$$3\chi_3\sigma_v = -2+2$$

$$3\chi_3\sigma_v = 0$$

$$\chi_3\sigma_v = 0$$

NOTE

Thus the complete set of characters of the irreducible representation is

C_{3V}	E	$2C_3$	$3\sigma_V$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

10.4 The great orthogonality theorem and character

This theorem is concerned with the elements of matrices constituting the irreducible representation of a point group. Let us consider two irreducible representations i and j of a point group. Let l_i and l_j be the dimensions of these representations, h is the order of the point group. R denotes a particular symmetry operation in the group. $(\Gamma_i(R))_{mn}$ is an element in the m^{th} row and n^{th} column of a matrix in the i^{th} irreducible representation. The complex conjugate of the element in the m'^{th} row and n'^{th} column of a matrix in the j^{th} irreducible representation is denoted by $(\Gamma_j(R))^*_{m'n'}$.

The elements $(\Gamma_i(R))_{mn}$ and $(\Gamma_j(R))^*_{m'n'}$ are related to h, l_i and l_j by the orthogonality theorem as follows.

$$\sum_R (T_i(R))_{mn} (T_j(R))^*_{m'n'} = (h / \sqrt{l_i l_j})\delta_{ij}\delta_{mm'}\delta_{nn'}$$

δ_{ij}, $\delta_{mm'}$, $\delta_{nn'}$ denote the kronecker delta symbols. The kronecker delta symbol δ_{ij} has the meaning $\delta_{ij} = 0$ for $i \neq j$ and $\delta_{ij} = 1$ for $i = j$. This theorem covers three cases.

1) If $(\Gamma_i(R))_{mn}$ and $(\Gamma_j(R))_{mn}$ represent two real elements

in the m^th row and n^th column of the matrix for the operation R in the representations i and j, then

$$h/\sqrt{l_i l_j})\delta_{ij} = 0\sum_R (T_i(R))_{mn}(T_j(R))_{mn} = (h/\sqrt{l_i l_j})\delta_{ij} = 0 \rightarrow (a)$$

The equation (a) can be applied to the irreducible representation of a group

containing the operations E and A. The matrix for the operations E and A in the two representations are given below:

$$E = \begin{bmatrix} E_{11} & E_{12} \\ E_{21} & E_{22} \end{bmatrix} \qquad A = \begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix}$$

$$E = \begin{bmatrix} E_{xx} & E_{xy} \\ E_{yx} & E_{yy} \end{bmatrix} \qquad A = \begin{bmatrix} A_{xx} & A_{xy} \\ A_{yx} & A_{yy} \end{bmatrix}$$

Equation (a) is applied to these representations.

Equation $E_{11}E_{xx} + A_{11}A_{xx} = 0$ is obtained as a result.

2) If $(\Gamma_i(R))_{mn}$ is the element in the m^th row and n^th column of a matrix for operation R in the i^th representation and $(\Gamma_j(R))_{mn}$ is the element in the m'^th row and n'^th column of a matrix for operation R in the same representation, then

$$\sum_R (T_i(R))_{mn}(T_j(R))_{m'n'} = (h/l_i)\delta_{mm'}\delta_{nn'} = 0$$

If $(\Gamma_i(R))_{mn}$ is the element in the m^th row and n^th column of a matrix for operation

R in the i^th irreducible representation, then

$$\sum_R ((T_i(R))_{mn})^2 = h/l_i$$

NOTE

10.5 Direct product representation

Suppose that R is an operation in the symmetry group of a molecule and X_1, X_2, X_3 ……. X_m and Y_1, Y_2 ….Y_n .are the two set of functions which are bases for representations of the group.

$$RX_i = \sum_{j=1}^{m} X_{ij} X_j$$

$$RY_k = \sum_{l=1}^{n} Y_{lk} Y_l$$

It is also true that

$$RX_i Y_k = \sum_{j=1}^{m} \sum_{l=1}^{n} X_{ij} Y_{lk} X_j Y_l$$

$$= \sum_j \sum_l Z_{jl,ik} X_j Y_l$$

Thus the set of functions X_iY_K, called the direct product of X_i and Y_k also forms a basis for a representation of the group. The $z_{il,ik}$ are the elements of a matrix of order (mn) x (mn).

We now have a very important theorem about the characters of the L matrices for the various operations in the group.

"The characters of the representations of a direct product are equal to the products of the characters of the representations based on the individual sets of functions".

The above theorem can be explained by taking the example C_3V point group. The direct product representations of the irreducible representations of a group can be obtained using the character table for the

group.

C_3V	E	$2C_3$	$3\sigma_V$
A_1	1	1	1
A_2	1	1	-1
A_3	2	-1	0

The direct product representation A_1A_2 is given by

	E	$2C_3$	$3\sigma_V$
	1x1	1x1	1x (-1)
A_1A_2	1	1	-1

Similarly, the direct product representations A,E,A_2E and E^2 are obtained as

	E	$2C_3$	$3\sigma_V$
A_1E	2	-1	0
A_2E	2	-1	0
E^2	4	1	0

The product representations A_1, A_2, A,E and A_2E are irreducible representations. The direct product representation E^2 is reducible.

The representation of a direct product, Γ_{AB}, will contain the totally symmetric representation only if the

irreducible Γ_A = irreducible Γ_B

NOTE

Let $\Gamma_A = \Gamma_B = A_2$ in C_3v group , then we get

$$\Gamma_{AB} = A_2 A_2 = A_1 \rightarrow (a)$$

Thus in equation (a), the product representation Γ_{AB} is totally symmetric.

10.6 Check Your Progress

1. What is meant by representation?
2. Define character table.
3. What is the concern of great orthogonality theorem?
4. How much elements represent in C_2V point group?

10.7 Answers To Check Your Progress Questions

1. Representation is a set of matrices which represent the operations of a point group. It can be classified in to two types, which are reducible representations and irreducible representations.

2. A character table is a 2 dimensional chart associated with a point group that contains the irreducible representations of each point group along with their corresponding matrix characters. It also contains the Mulliken symbols used to describe the dimensions of the irreducible representations, and the functions for symmetry symbols for the Cartesian coordinates as well as rotations about the Cartesian coordinates.

3. This theorem is concerned with the elements of matrices constituting the irreducible representation of a point group.

4. C_2V point group consists of 4 elements such as E, C_2, σ_{vxz} and σ_{vyz}, each is in a separate class.

10.8 Summary

- In this unit describes the character table for a group can be constructed with the properties of irreducible representation. It can be found from the great orthogonality theorem.
- This unit is concerned with the elements of matrices constituting the irreducible representation of a point group. It can expressed in

the best way for our understanding.

NOTES

10.9 Keywords

- Types of representation - reducible representations and irreducible representations.
- Character table - It is a 2 dimensional chart associated with a point group that contains the irreducible representations of each point group along with their corresponding matrix characters.
- C_2V point group - It consists of 4 elements such as E, C_2, σ_{vxz} and σ_{vyz}, each is in a separate class.

10.10 Self-Assessment Questions and Exercises

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1. Give a brief review about reducible and irreducible representations.
2. Give a brief review about Character table of C2v and C3v point groups.
3. Explain about the great orthogonality theorem.
4. Explain direct product representation.

10.11 Further Readings

1. **Chemical Application of Group Theory**, F.A. Cotton, John Wiley and Sons Inc. New York,1971.
2. **Group theory and its applications to Chemistry**, K.V. Raman, Tata McGraw-Hill Publishing Company,1990.
3. **Irreversible Thermodynamics,** J. Rajaram and J.C. Kuriacose, Lal Nagin Chand, New Delhi, 1989.

Unit 11 Symmetry oriented spectral methods

NOTE

UNIT -11 Symmetry oriented spectral methods

Structure

11.0 Introduction

Group theory is an important component for understanding the fundamentals of vibrational spectroscopy. The molecular or solid state symmetry of a material in conjunction with group theory form the basis of the selection rules for infrared absorption and Raman scattering. In this unit we learn about the Application of group theory to IR and Raman spectra - H_2O and NH_3 molecules and application of group theory to electronic spectra (HCHO and C_2H_4)

11.1 Objectives

After going through this unit, you will be able to;

- ✓ To know the Application of group theory to IR and Raman spectra - H_2O and NH_3 molecules
- ✓ Understand the Application of group theory to electronic spectra (HCHO and C_2H_4)

11.2 Application of group theory to IR and Raman spectra - H2O and NH3 molecules

It is not necessary for a molecule to have a permanent electric dipolemoment for IR absorption. But during the absorption, there must be a change in the dipolemoment of the molecule. This change in the dipole moment can be predicted in terms of symmetry using group theory. For this purpose direct product representation of the functions involved in the transition moment integral must be

determined. If the value of the integral is non-zero, the transition is allowed and if it is equal to zero, it is forbidden.

The transition moment integral is given by

$$P = \int \phi_V^g P^{\wedge} \phi_V^i \, d\tau$$

Φ_V^g and Φ_v^i are the wavefunctions of the ground and i[th] excited state of the vibrational level.

$P^{\wedge}$ is the electrical dipolemoment operator.

Since dipolemoment is a vector quantity and also it is the product of charge and distance between the charges, it can be written as,

$$P = P_x + P_y + P_z$$

$$P_x = e\int \phi_V^g x \phi_V^i \, d\tau$$

$$P_y = e\int \phi_V^g y \phi_V^i \, d\tau$$

$$P_z = e\int \phi_V^g z \phi_V^i \, d\tau$$

where, 'e' is the charge and x,y and z are the distances in the respective directions.

The value of the above integrals in general can be obtained by considering the symmetries, of the functions involved in the integral. Taking P_n as an example, the direct product representation of Φ_V^g , X and Φ_V^j must be totally symmetric in order that $P_x \neq 0$.

Since Φ_V^g is always totally symmetric, Φ_V^i must have the same symmetry that of x. In general the symmetry corresponding to excited mode of vibration (Φ_V^i) must match with the symmetry of any one of the Cartesian coordinates x,y and z for a molecule to be IR active. The above concept can be applied in the case of H_2O and NH_3 molecules.

WATER MOLECULE

There are three vibrational modes in the water molecule. Two of them have A_1 symmetry and one has B_2 symmetry. Using group theory, it is possible to predict which of them are IR active.

A_1 mode:

P_x: Direct product of $\Gamma_g\, \Gamma_x\, \Gamma_i = A_1B_1A_1 = B_1\ \therefore P_x = 0$

P_y: Direct product of $\Gamma_g\, \Gamma_y\, \Gamma_i = A_1B_2A_1 = B_2\ \therefore P_y = 0$

P_z: Direct product of $\Gamma_g\, \Gamma_z\, \Gamma_i = A_1\, A_1\, A_1 = A_1\ \therefore P_z \neq 0$

Thus A_1 mode in water is IR active since $P_z \neq 0$

B_2 mode:

P_x: Direct product of $\Gamma_g\, \Gamma_x\, \Gamma_i = A_1B_1B_2 = A_1A_2 = A_2\ \therefore P_x = 0$

P_y: Direct product of $\Gamma_g\, \Gamma_y\, \Gamma_i = A_1B_2\, B_2 = A_1A_1 = A_1\quad \therefore P_y \neq 0$

P_z: Direct product of $\Gamma_g\, \Gamma_z\, \Gamma_i = A_1\, A_1\, B_2 = B_2\ \therefore P_z = 0$

Therefore B_2 mode is also IR active since $P_y \neq 0$

AMMONIA MOLECULE

Ammonia molecule has four modes of vibrations, two of them have A_1 symmetry and the other two have E symmetry.

A_1 mode:

In the case of NH_3, the coordinates X and Y together transforms into E representations.

P_xP_y : Direct product of $\Gamma_g\, \Gamma_{x,y}\, \Gamma_i = A_1EA_1 = E\ \therefore P_x\, P_y = 0$

P_z: Direct product of $\Gamma_g\, \Gamma_z\, \Gamma_i = A_1\, A_1\, A_1 = A_1\ \therefore P_z \neq 0$

Since $P_z \neq 0$, A_1 mode is IR active.

E mode:

P_xP_y : Direct product of $\Gamma_g\, \Gamma_{x,y}\, \Gamma_i = A_1EE = E^2$ (4 1 0)

(4 1 0) corresponds to the characters of the reducible representations. This can be split into various irreducible representations using standard reduction formula. Such an attempt shows that $E^2 = A_1 + A_2 + E$.

Since A_1 forms a part of the $P_{x,y}$ must be totally symmetric.

$$\therefore P_xP_y \neq 0$$

P_z :Direct product of $\Gamma_g \Gamma_z \Gamma_i = A_1 A_1 E = E$

$$\therefore P_z = 0$$

Since we found that $P_x P_y \neq 0$, E mode is also IR active.

It is therefore observed that all the four modes of NH_3 molecule are IR active and all the three modes of H_2O molecule are IR active.

APPLICATIONS OF GROUP THEORY TO VIBRATIONAL RAMAN SPECTRA

A charge in the dipolemoment causes the molecule to be IR-active. The change in the induced dipolemoment causes the molecule to be Raman active.

The induced dipolemoment is defined as

$$\mu_i = \alpha E$$

where, α = polarisibility, E = Electric field strength

Since a change in the induced dipolemoment will result in the change in the polarisibility, a molecule shows Raman spectra. If there is a change in the polarisibility due to the absorption of radiation. In order to apply group theory to Raman spectra, the value of the transition moment integral has to be calculated. The integral is given as,

$$\gamma_i = \int \phi_V^y \alpha^{\wedge} \phi_V^i d\tau$$

where $\alpha^{\wedge}$ = polarisibility operator

The polarisibility operator is a measure of the quadratic functions of the cartesian coordinates (x^2, y^2, z^2, xy,yz,zx). For a molecule to be Raman active, the normal vibration should have the same irreducible representation as any one of the quadratic functions of the Cartesian coordinate. In other words, the direct product representation of any one of the following should be totally symmetric.

NOTE

$\Gamma_1\, \Gamma_{xy}\, \Gamma_2$	$\Gamma_1\, \Gamma_{x2}\, \Gamma_2$
$\Gamma_1\, \Gamma_{xz}\, \Gamma_2$	$\Gamma_1\, \Gamma_{y2}\, \Gamma_2$
$\Gamma_1\, \Gamma_{yz}\, \Gamma_2$	$\Gamma_1\, \Gamma_{z2}\, \Gamma_2$

[Γ_1 is always A_1]

This can be verified by considering water and ammonia molecule.

WATER MOLECULE

There are three vibrational modes for water molecule. Their representations are:

$$T_{vib} = 2A_1 + B_2$$

A_1 mode

In order to find out the vibrational mode due to 'A_1' is Raman active or not, the direct product representations for the following are determined.

$\Gamma_1\, \Gamma_{xy}\, \Gamma_2 = A_1 A_2 A_1 = A_2$	$\Gamma_1\, \Gamma_{x2}\, \Gamma_2$
$\Gamma_1\, \Gamma_{xz}\, \Gamma_2 = A_1 B_1 A_1 = B_1$	$\Gamma_1\, \Gamma_{y2}\, \Gamma_2 = A_1\, A_1\, A_1 = A_1$
$\Gamma_1\, \Gamma_{yz}\, \Gamma_2 = A_1 B_2 A_1 = B_2$	$\Gamma_1\, \Gamma_{z2}\, \Gamma_2$

It is noted that, among the 6 representations, three are totally symmetric. Therefore, A_1 mode is Raman active.

B_2 mode

In a similar way the direct product representations involving 'B_2' mode are determined as follows:

$\Gamma_1\ \Gamma_{xy}\ \Gamma_2 = A_1A_2B_2 = B_1$

$\Gamma_1\ \Gamma_{yz}\ \Gamma_2 = A_1B_2B_2 = A_1$

$\Gamma_1\ \Gamma_{xz}\ \Gamma_2 = A_1B_1B_2 = A_2$

$\Gamma_1\ \Gamma_{x2}\ \Gamma_2$

$\Gamma_1\ \Gamma_{y2}\ \Gamma_2 = A_1\ A_1\ B_2 = B_2$

$\Gamma_1\ \Gamma_{z2}\ \Gamma_2$

It is observed that only one among the six leads to totally symmetric representation. Therefore B_2 mode is also Raman active.

AMMONIA MOLECULE

There are four vibrational modes in ammonia molecule. In terms of group theory, their representations have been known to be $2A_1 + 2E$; Group theory i, applied to verify whether theses modes are active or not.

A_1 mode

The direct product representation corresponding to 'A_1' mode is determined in the case of the following,

$\Gamma_1\ \Gamma_{xy}\ \Gamma_2$

$\Gamma_1\ \Gamma_{xz}\ \Gamma_2 = A_1\ E\ A_1 = E$

$\Gamma_1\ \Gamma_{yz}\ \Gamma_2 = A_1\ E\ A_1 = E$

$\Gamma_1\ \Gamma_{x2}\ \Gamma_2$
$\Gamma_1\ \Gamma_{y2}\ \Gamma_2$

$\Gamma_1\ \Gamma_{z2}\ \Gamma_2 = A_1\ A_1\ A_1 = A$

Among these, only one is totally symmetric and there is no way of finding out the representation for three of them (xy, x^2, y^2)

E mode

The direct product representation corresponding to 'E' mode is determined in the case of the following.

$\Gamma_1\ \Gamma_{xy}\ \Gamma_2\} = A_1EE = E^2$

$\Gamma_1\ \Gamma_{yz}\ \Gamma_2\}$

$\Gamma_1\ \Gamma_{z2}\ \Gamma_2 = A_1A_1E = E$

Unit -11
Symmetry oriented spectral methods

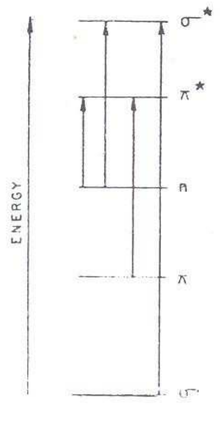
NOTES

The result shows that one representation is not totally symmetric and the other two gives a reducible representation (E^2 = 4 1 0). This reducible representation can be split into number of representations and among them one is totally symmetric. Therefore 'E' mode is called Raman active.

In the case of water and ammonia molecule, the corresponding vibrational modes are both IR and Raman active. But in the case of centro symmetric molecules (molecules having centre of symmetry) like CO_2, acetylene, N_2F_2, if the vibrational modes are Raman active then they will be IR inactive and vice versa. This statement is known as mutual exclusion group.

6.2 Application of group theory to electronic spectra (HCHO and C2H4)

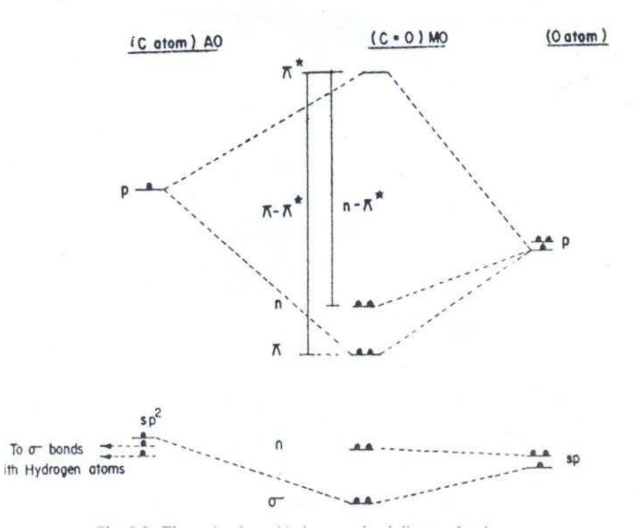
UV, Visible or electronic spectroscopy is mainly applicable to organic molecules. In such cases, transitions occurs between electronic energy levels. In the case of molecules, the electronic energy levels, correspond to molecular orbital energy levels. The various molecular orbitals are σ and π (bonding molecular orbitals), σ^* and π^* (antibonding molecular orbitals), n (non-bonding). The energy level diagram for these orbitals are shown in the figure,



Group theory can be applied to electronic spectroscopy by

considering HCHO (formaldehyde) molecule as an example. Before we apply this theory, the molecular orbital energy diagram for the carbonyl group -C=O of formaldehyde should be taken in to consideration.

The diagram is shown in the figure.



The possible transition are n-π^* and π-π^*.

By applying group theory, it is possible to find out which type of transition is allowed or not. For the electronic transitions to be allowed, the following integrals must take non-zero value.

$$\int \phi_g x \phi_i d\tau$$

$$\int \phi_g y \phi_i d\tau$$

$$\int \phi_g z \phi_i d\tau$$

where, Φ_g and Φ_i are the wave functions for the ground state and excited states respectively.

For the integral to take non-zero value, the direct product representation of Φ_g and Φ_i

must have the same symmetry as that of any one of the Cartesian coordinates namely x, y, z.

n-π* transition:

The arrangement of electrons in the ground and excited state during this type of transition is shown below.

$$\phi_g = (\pi^2)(n^2)$$

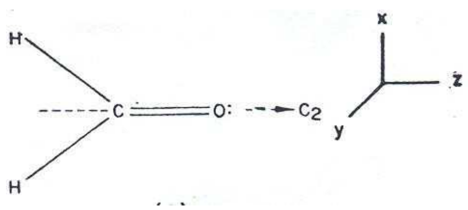
$$\phi_i = (\pi^2)(n)(\pi^*)$$

An electron in a molecular orbital has a particular irreducible representation. If the two electrons remain in the same orbital, the product of these representation is always totally symmetric. Therefore it will corresponds to 'A_1' representation. In such a case, the ground state representation is given as

$$T_g = A_1 A_1 = A_1$$

In the excited state wave function, we find that there is one electron each in the non-bonding and π- antibonding orbitals. In order to find out the representations corresponding to the electrons in n and π^* orbitals, the shapes of these orbitals should be considered.

The figure shows the shapes of π, π^* and n orbitals.



Formaldehyde molecule belong, to C_2V point group. The various operations present in this group are E, C_2, σ_{xz} and σ_{yz}. These operations should be performed on π, π^* and n orbitals in order to find out the characters corresponding to each operation. Such an attempt leads to the following table. The last column of the

table gives the Mulliken symbol for each orbital.

	E	C_2	σ_{xz}	σ_{yz}	Mulliken symbol
N	1	-1	-1	1	B_2
π^*	1	-1	1	-1	B_1
π	1	-1	1	-1	B_1

Based on this table, the representation for the excited state is given as

$$T_i = A_1B_2B_1 = A_2$$

∴ The direct product representation for the ground and excited state is $A_1.A_2 = A_2$.

But this representation (A_2) does not correspond to the representation of any one of the Cartesian coordinates. This shows that all the integrals take the value equal to zero, and hence n-π^* transition is not electronically allowed.

But n-π^* has been found to be magnetically allowed. The integrals corresponding to the components of the magnetic dipolemoment operator are given below,

$$\int \phi_g \mu(x) \phi_i d\tau$$

$$\int \phi_g \mu(y) \phi_i d\tau$$

$$\int \phi_g \mu(z) \phi_i d\tau$$

The representation for the $\mu_{(x)}$, $\mu_{(y)}$, $\mu_{(z)}$ are R_x,R_y and R_z which corresponds to B_2, B_1 and A_2 respectively. Since the direct product representation of Φ_g and Φ_i is A_2 as seen earlier which corresponds to one of the representations here. ∴ one of the integrals take non-zero value and hence n-π^* transition is magnetically allowed. But the signal corresponding to this

transition will be very weak because the interaction of the electric component of electromagnetic radiation with formaldehyde will be very much greater than that of the magnetic component.

π-π* transition:

The arrangement of electrons in the excited state is

$$\Phi_i = (n)\ (n^2)\ (\pi^*)$$

By a similar argument the representation corresponding to excited state is arrived at

$$T_i = B_1\, A_1\, B_1 = A_1$$

∴ The direct product representation of the ground and excited state is

$$A_1\ A_1\ = A_1$$

This direct product representation corresponds to the representation of the z-axis.

∴ One of the integrals take non-zero value.

Hence π-π* transition is electronically allowed.

11.4 Check Your Progress

1. Define n-π* transition
2. How to prove water IR active?
3. What are transition present in UV, Visible or electronic spectroscopy?

11.5 Answer To Check Your Progress

1. The arrangement of electrons in the ground and excited state during this type of transition is shown below.

$$\phi_g = (\pi^2)(n^2)\quad \phi_i = (\pi^2)(n)(\pi^*)$$

2. There are three vibrational modes in the water molecule. Two of them have A_1 symmetry and one has B_2 symmetry. Using group theory, it is possible to predict which of them are IR active.

3. UV, Visible or electronic spectroscopy is mainly applicable to

organic molecules. In such cases, transitions occurs between electronic energy levels. In the case of molecules, the electronic energy levels, correspond to molecular orbital energy levels. The various molecular orbitals are σ and π (bonding molecular orbitals), σ^* and π^* (antibonding molecular orbitals), n (non-bonding

NOTES

11.6 SUMMARY

- Spectroscopy studies like IR and Raman the interaction of light and matter. The symmetry operations of a molecule form a mathematical group. Matrices that multiply the same way as the members of a group form a representation of the group.
- Acorrding to this reducible representation can be split into number of representations and among them one is totally symmetric . where the characters are the traces of the matrices of the representations.

11.7 Keywords

IR absorption - It is not necessary for a molecule to have a permanent electric dipolemoment for IR absorption.
Electronic spectroscopy - UV, Visible or electronic spectroscopy is mainly applicable to organic molecules. In such cases, transitions occurs between electronic energy levels

11.8 Self Assessment Questions And Exercises

1. Define application of group theory to IR and Raman spectra?
2. Explain application of group theory to electronic spectra (HCHO and C_2H_4)

11.9 Further Reading

1. **Chemical Application of Group Theory**, F.A. Cotton, John Wiley and Sons Inc. New York,1971.
2. **Group theory and its applications to Chemistry**, K.V. Raman, Tata McGraw-Hill Publishing Company,1990.

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NOTE

BLOCK – 4:
CHEMICAL KINETICS
Unit-12: REACTIONS IN SOLUTION

Structure

12.0 Introduction

Chemistry, by its very nature, is concerned with change. Substances with well-defined properties are converted by chemical reactions into other substances with different properties. For any chemical reaction, chemists try to find out

a) The feasibility of a chemical reaction which can be predicted by thermodynamics (as you know that a reaction with $\Delta G < 0$, at constant temperature and pressure is feasible);

b) (b) extent to which a reaction will proceed can be determined from chemical equilibrium;

c) (c) speed of a reaction i.e. time taken by a reaction to reach equilibrium.

Along with feasibility and extent, it is equally important to know the rate and the factors controlling the rate of a chemical reaction for its complete understanding. For example, which parameters determine as to how rapidly food gets spoiled? How to design a rapidly setting material for dental filling? Or what controls the rate at which fuel burns in an auto engine? All these questions can be answered by the branch of chemistry, which deals with the study of reaction rates and their mechanisms, called chemical kinetics. The word kinetics is derived from the Greek word 'kinesis' meaning movement. Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction. For example, thermodynamic data indicate that diamond shall convert to graphite but in reality the conversion rate is so

NOTE

slow that the change is not perceptible at all Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates can be altered. The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction. At the macroscopic level, we are interested in amounts reacted or formed and the rates of their consumption or formation. At the molecular level, the reaction mechanisms involving orientation and energy of molecules undergoing collisions, are discussed. In this Unit, we shall be dealing with average and instantaneous rate of reaction and the factors affecting these. Some elementary ideas about the collision theory of reaction rates are also given. However, in order to understand all these, let us first learn about the reaction rate.

SOLUTION KINETICS

When a reaction takes place in solution

- The solvent is in larger than the reactant
- Solvent concentration is constant during the course of reaction.
- Theories of solution kinetics are more complicated than gas phase.
- In solutions the collision between the reactants are termed as encounter.
- Some of the reaction has same rate in solution phase as well as gas phase Eg: N_2O_5, O_3 decomposition etc.

The rate of reaction in gas phase and solution phase are equal only in ideal solution

12.1 Objectives

After going through this unit, you will be able to:

- Understand about the kinetics and rate of the reaction
- Understand the reaction rate in solution
- Explain the concept of Bronsted and Bjerrum equation

12.2 REACTIONS IN SOLUTION

There are many reactions which take place more or less at the same rate in gaseous and solution phases (e.g. decomposition of CH_2I-CH_2I and N_2O_5 in CCl_4 solvent; isomerization of d-pinene). This shows that the reactions proceed by the same mechanism in both the phases. There are however many exceptions.

Example: the reaction between $(C_2H_5)_3N$ and C_2H_5Br to give a quaternary ammonium salt is considerably faster in polar solvents like nitrobenzene than in non-polar solvents or in the gaseous phase. The activated complex in the reaction is more polar than the reactants.

NOTE

12.3 FACTORS WHICH INFLUENCE THE REACTION RATE IN SOLUTION

(i) For ionic reaction

A. Reaction between an ion and molecule the Arrhenius frequency factor has normal value.

B. Reaction between same sign, the value of “A” is much lower.

C. Reaction between opposite sign, higher the value of “A”. Hence the frequency factor is the direct measure of rate of the reaction.

(ii) Approaching of species to each other

Rate of approaching of reacting species to each other depend upon the rate of diffusion of the two species through solvent diffusion-controlled process that are very fast. The diffusion-controlled process depends upon the viscosity of the medium. In low viscous medium, higher the diffusion takes place.

(iii) Cage effect

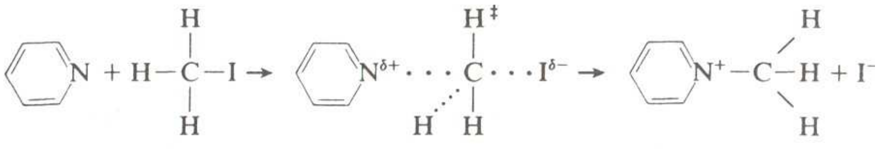
The reactant species after the collision are held together by solvent species for about 10^{-8} to 10^{-10}s. During this time lag, the reacting molecules collide with each other or make a suitable direction for the favorable reaction to take place. The reacting molecule held together for a period of time by solvent cage is said to be cage effect or frank-Rabinowitch effect.

(iv) Energy and orientation of reacting species

This is controlled by the nature of species. In general, the reaction would be fast in a solution in which the activated complex is more stable. Activated complex is more stable in polar solvent when it is polar and vice versa.

(v) Effect of Solvation

Solvation is based on polarity, higher the dipole will more solvated by polar solvent.



Here, products are two separate ions and activated complex has partial charge as above. In polar solvent such as nitrobenzene there is more solvation of activated complex than the reactant. The effect of solvation lowers the activity co-efficient of activated

NOTE

complex ($\gamma^{\pm} a^{\neq}$) and thus rate become high.

On the other hand,

$$Y^{*} + RX^{+} \Leftrightarrow \left(Y^{\delta^-} \ldots\ldots\ldots\ldots R \ldots\ldots\ldots X^{\delta^+}\right) \rightarrow YR + X$$

Here, there is decrease in polarity as the activated complex is formed. Activated complex is less solvated than reactant in polar solvent. And thus, decreases the rate.

12.4 APPLICATION OF ARRT TO SOLUTION KINETICS

For a general bimolecular reaction,

$$A + B \Leftrightarrow \qquad X^{\neq} \rightarrow \text{Product}$$

$$k^{\neq} = \frac{a^{\neq}}{a_A \cdot a_B} \left(\therefore a = activity\right)$$

$$K^{\neq} = \frac{\gamma^{\neq} C^{\neq}}{\gamma_A C_A \cdot \gamma_B C_B} \rightarrow (1)$$

$$C^{\neq} = K^{\neq} \frac{\gamma_A \gamma_B}{\gamma^{\neq}} \cdot C_A C_B \rightarrow (2)$$

Rate of the reaction is rate of decomposition of activated complex i.e.,$X^{\neq} \rightarrow$ P

$X^{\neq}$ must have one of its vibrational degrees of freedom which would be highly unstable. This is responsible for the decomposition of $X^{\neq}$ in product.

$$\text{Rate} = \gamma\left[C^{\neq}\right]$$

γ = frequency of vibration

$$= \gamma K^{\neq} \frac{\gamma_A \gamma_B}{\gamma^{\neq}} \cdot C_A C_B \rightarrow (3)$$

Any simple bimolecular reaction in solution

$$\text{Rate} = K_s C_A C_B \rightarrow (4)$$

Equation (3) = (4)

$$K_S C_A C_B = \gamma K^{\neq} \frac{\gamma_A \gamma_B}{\gamma^{\neq}} C_A C_B$$

$$K_S = \gamma K^{\neq} \frac{\gamma_A \gamma_B}{\gamma^{\neq}} \rightarrow (5)$$

According to Boltzmann equation

$$h\gamma = K_B T$$

$$\gamma = \frac{K_B T}{h}$$

NOTE

Substitute in equation (5)

$$K_S = \frac{K_B T}{h} \frac{\gamma_A \gamma_B}{\gamma^{\neq}} K^{\neq} \rightarrow (6)$$

For ideal solution γ_A, γ_B ,$\gamma^{\neq}$ =1

$$K_g = \frac{K_B T}{h} K^{\neq} \quad \text{hence}$$

$$K_S = K_g \frac{\gamma_A \gamma_B}{\gamma^{\neq}} \rightarrow (7)$$

For unimolecular reaction, $K_S = K_g \frac{\gamma_A}{\gamma^{\neq}}$

have the solvation of reactant and activated complex are almost same both are having almost similar structure, then

$$K_s = K_g$$

Example: chemisorption of N_2O_5, O_3.

12.5 BRONSTED - BJERRUM EQUATION

Bronsted Bjerrum explain the relationship between ionic strength and rate of a chemical reaction in solution. And this effect is involved in non catalytic reaction.

For a general reaction,

$$A^{ZA} + B^{ZB} \underset{K_2}{\overset{K_1}{\leftrightarrow}} AB^{(ZA+ZB)\neq} \xrightarrow{K_3} \text{Product}$$

$$\overset{\neq}{k} = \frac{C^{\neq}_{AB}}{C_A C_B} \frac{\gamma^{\neq}_{AB}}{\gamma_A \gamma_B} \text{ -------- (1)}$$

$$C^{\neq}_{AB} = K^{\neq} \frac{\gamma_A \gamma_B}{\gamma^{\neq}_{AB}} .C_A .C_B \text{ ------- (2)}$$

$$\frac{dp}{dt} = k_3 C^{\neq}_{AB} = k_3 k^{\neq} C_A C_B \frac{\gamma_A \gamma_B}{\gamma^{\neq}_{AB}} \text{ ----- (3)}, \quad k_3 k^{\neq} = k_0$$

$$\gamma = k_0 \left(\frac{\gamma_A \gamma_B}{\gamma^{\neq}_{AB}} \right) C_A C_B \text{ ------- (4)}$$

$$\left(\frac{\gamma_A \gamma_B}{\gamma^{\neq}_{AB}} \right) = \text{kinetic activity factor}$$

For a reaction, A + B $\rightarrow$ P

$$\gamma = K_r\, C_A\, C_B \text{ -------- (5),} \quad \text{Equating (4) \& (5)}$$

$$k_r C_A C_B = K_0 \frac{\gamma_A \gamma_B}{\gamma^{\neq}_{AB}} . C_A . C_B \quad , \quad k_r = k_0 \frac{\gamma_A \gamma_B}{\gamma^{\neq}_{AB}} \text{------------(6)}$$

Taking log on both sides,

$$\log k_r = \log k_0 + \log \gamma_A + \log \gamma_B - \log \gamma^{\neq}_{AB} \quad (6\text{ A})$$

According to Debye Huckel theory of strong electrolyte the activity coefficient

related with ionic strength as $\log \gamma_i = -AZ^2_i \sqrt{\mu}$

A- constant = 0.51dm$^{-3/2}$ mol ^{½} for aqueous solution at 25^{0}c

Z_i = charge of ‘i ’th ion

$$\mu = \frac{1}{2} \sum C_i Z_i^2 \qquad C_i = \text{concentration, } Z_i = \text{valencies of species}$$

Thus $\log \gamma_A = -AZ_A^2 \sqrt{\mu}$ ------- (7)

$$\log \gamma_B = -AZ_B^2 \sqrt{\mu} \text{ ------- (8)}$$

$$\log \gamma^{\neq}_{AB} = -A(Z_A + Z_B)^2 \sqrt{\mu} \text{ -------- (9)}$$

Substitute equations (7), (8) and (9) in equation 6(A)

$$\log \frac{k_r}{k_0} = -AZ_A^2 \sqrt{\mu} - AZ_B^2 \sqrt{\mu} + A(Z_A + Z_B)^2 \sqrt{\mu}$$

$$= -A\sqrt{\mu} \left[Z_A^2 + Z_B^2 - (Z_A + Z_B)^2 \right]$$

$$= -A\sqrt{\mu} \left[Z_A^2 + Z_B^2 - Z_A^2 - Z_B^2 - 2Z_A Z_B \right]$$

$$\log \frac{k_r}{k_0} = +A.2Z_A Z_B \sqrt{\mu}$$

For an aqueous solution at 25°C this equation becomes

$$\log \frac{k_r}{k_0} = 1.02 Z_A Z_B \sqrt{\mu}$$

when ionic strength is zero, $k_r = k_0$ .This equation is known as Bronsted Bjerrum

NOTE

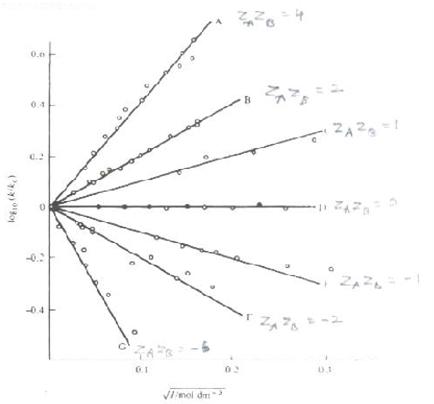
equation. This equation shows that variation of 'k' with $\sqrt{\mu}$ depends on $Z_A Z_B$.

The plot of log k_r/k_0 vs $\sqrt{\mu}$ will be linear.

Case (i)

When $Z_A Z_B = 0$ i.e. one of the reactant is zero charge (i.e. non electrolyte)

Log k_r = log k_0, hence increase of $\sqrt{\mu}$ has no effect on $\log \frac{k_r}{k_0}$.



Eg: $[Cr(urea)_3]^{3+} + 6H_2O \rightarrow [Cr(H_2O)_3]^{3+} + 3urea$, $Z_A = 3$, $Z_B = 0$

$$CH_2ICOOH + CNS^- \rightarrow CH_2(CNS)CNH + I^-$$

Case (ii)

When $Z_A Z_B$ = +ve, $Z_A Z_B$ both has same size. $\log \frac{k_r}{k_0}$ increases with increasing $\sqrt{\mu}$, $S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-}$, $Z_A, Z_B = 2$

NOTE

$$2[Co(NH_3)_5Br] + Hg^{2+} + 2H_2O \rightarrow 2[Co(NH_3)_5H_2O] + HgBr_2$$

$Z_A, Z_B = 4$

Case (iii)

When Z_AZ_B = -ve $\log\frac{k_r}{k_0}$ decreases with increasing $\sqrt{\mu}$

(i) $H_2O_2 + 2Br^- + 2H^+ \rightarrow 2H_2O + Br_2 \quad Z_A, Z_B = (-1)(1) = -1$

$[Co(NH_3)Br]^{2+} + OH^- \rightarrow [Co(NH_3)OH] + Br^- \quad Z_A, Z_B = -2$

12.6 Check Your Progress

1. What is mean by rate of the reaction?
2. How does the rate of reaction depend on volume?
3. Explain Enzyme catalysts?

12.7 Answers to Check Your Progress Questions

1. The rate of a reaction is the speed at which a chemical reaction happens. If a reaction has a low rate, that means the molecules combine at a slower speed than a reaction with a high rate. Some reactions take hundreds, maybe even thousands, of years while others can happen in less than one second.

2.The rate of reaction r for the reaction A→B is given by : r=k[A],where k is the rate constant and [A] is the concentration of the reactant.(I've assumed the reaction to follow first order kinetics.)So r is directly proportional to the concentration of the reactant. rate increases on increasing reactant concentration. However, the concentration of A is actually in moles/Liter, which is moles per unit volume. Hence, r is inversely proportional to the volume and the rate decreases on increasing volume of the reaction vessel.

3. Enzyme catalysis is the increase in the rate of a process by a biological molecule, an "enzyme". Most enzymes are proteins, and most such processes are chemical reactions. Withinthe enzyme, generally catalysis occurs at a localized site, called the active site.

12.8 Summary

- ✓ Chemical kinetics is the study of chemical reactions with respect to reaction rates, effect of various variables, rearrangement of atoms and formation of intermediates.
- ✓ The rate of a reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed Application of ARRT to solution kinetics,
- ✓ Mathematical representation of Bronsted Bjerrum equation.It has to be determined experimentally and cannot be predicted.

12.9 Keywords

NOTE

Cage Effect: The **cage effect** in chemistry describes how the properties of a molecule are affected by its surroundings. First introduced by Franck and Rabinowitch in 1934, the **cage effect** suggests that instead of acting as an individual particle, molecules in solvent are more accurately described as an encapsulated particle.

Solvation effect: If the polarity of the product is different from that of the starting material, **solvation** changes the thermodynamic properties of the reaction. If the transition state experiences the change in polarity (usually charge buildup), **solvation** changes the **kinetics** properties of the reaction

12.10 Self-assessment questions and exercises

1. Explain in detail about the rate constants.
2. Discuss in detail about reaction rates in solution
3. Distinguish the Bronsted and Bjerrum equation

12.11 Further readings

1. C.M. Guldberg and P. Waage,"Studies Concerning Affinity" *Forhandlinger i Videnskabs-Selskabet i Christiania* (1864), 35

2. P. Waage, "Experiments for Determining the Affinity Law" ,*Forhandlinger i Videnskabs-Selskabet i Christiania*, (1864) 92.

3. C.M. Guldberg, "Concerning the Laws of Chemical Affinity", *Forhandlinger i Videnskabs-Selskabet i Christiania* (1864) 111

NOTE

Unit-13 Salt Effect

Structure

13.0 Introduction

In our last two modules, we took up solution kinetics in detail. You now know that solution kinetics is the kinetic study of chemical reactions taking place in solution phase and the nature of solvent has a predominant influence on the kinetics of such reactions.

In general, the solution phase reactions can be classified as Ionic reactions and Non Ionic reactions. And here, we are concerned with the kinetic study of ionic reactions.

$$A + B \rightarrow P \quad \ldots(1)$$

$$Rate = k[A][B] \quad \ldots(2)$$

where k is the rate constant for the reaction.

We found that only Classical Thermodynamic approach of transition state theory can be utilized to determine the rate constant of ionic reactions or solution phase reactions and studied the effect of solvent on rate constant. In this module, focus will be laid on primary salt effect and secondary salt effect.

13.1 Objectives

After going through this unit, you will be able to:

- Understand the concept behind the salt effect in the solution.
- Understand the mechanisms behind effect of pressure and volume of activation in solution.
- Learn about the Effect of substituents on reaction rates

NOTE

13.2 PRIMARY SALT EFFECT

By doing a neutral salt to the reaction mixture having either type of ions, the rate of the reaction is considerably affected according to the Bronsted Bjerrum equation is said to be primary salt effect or neutral salt effect.

It is experimentally found that the rates of second-order reactions between charged species are affected strongly by the ionic strength of the solution, this quantity being defined as

$$I = 1/2\sum C_j Z_j^2$$

where C_j is the concentration of each ion present in the solution and Z_j is the charge number of the ion. When the reacting ions are of same sign, increase in ionic strength increases the rate whereas when the reacting ions are of opposite signs, increase in ionic strength decreases the rate.

13.3 SECONDARY SALT EFFECT

This arises if one of the reactants is a weak electrolyte that can be stimulated by catalytic reaction. The rate of the reaction depends upon the amount of salt added in a catalytic reaction. Actual change in concentration of reacting ion by adding the salt externally.

This effect is not having a direct influence. But it will influence the concentration of reactant. The equilibrium constant for the dissociation of weak acid HA can be written as

$$k_a = \frac{[H^+][A^-]}{[HA]} \frac{\gamma_{H^+}\gamma_{A^-}}{\gamma_{HA}}$$

Addition of salt will influence the activity co-efficient they also influence the concentrations of H+, A- and HA and this way the catalytic activity has been lowered/increased, will influence rate is said to be secondary salt effect.

13.4 INFLUENCE OF INTERNAL PRESSURE

We know the rate constant in solution has the relationship with gas phase rate equation.

$$K_s = \frac{K_B T}{h} K^{\neq} \frac{\gamma_A \gamma_B}{\gamma^{\neq}} \rightarrow (1)$$

$$K_o = \frac{K_B T}{h} K^{\neq} \rightarrow (2)$$

K_o = rate constant under ideal conditions.

For an ideal solution $\gamma_A \neq \gamma_B \neq \gamma^{\neq} \neq 1$

activity co-efficient according to langmuir is given by

$$RT \ln \gamma_1 = V_1 \left(P_1^{1/2} - P_2^{1/2}\right)^2$$

$$\gamma_1 = V_1 \Delta$$

V_1 – Molar volume

P_1 – Pressure of solvent

P_2 – Pressure of solute

$$RT \ln \gamma_1 = V_1 \Delta \rightarrow (3)$$

$$RT \ln \gamma_A = V_A \Delta_A; \quad RT \ln \gamma_B = V_B \Delta_B; \quad RT \ln \gamma^{\neq} = V^{\neq} \Delta^{\neq}$$

$$RT \ln \gamma_A + RT \ln \gamma_B - RT \ln \gamma^{\neq} = V_A \Delta_A + V_B \Delta_B - V^{\neq} \Delta^{\neq}$$

$$RT \ln \left(\frac{\gamma_A \gamma_B}{\gamma^{\neq}}\right) = V_A \Delta_A + V_B \Delta_B - V^{\neq} \Delta^{\neq}$$

$$RT \ln \frac{K_s}{K_o} = V_A \Delta_A + V_B \Delta_B - V^{\neq} \Delta^{\neq}$$

The molar volume of reactant and activated complex are equal.

Case (i)

$$\text{If } \Delta_A = \Delta_B \approx \Delta^{\neq}$$

Then the solvent will not affect the rate of reaction in solution.

Case (ii)

$$P_{solvent} \approx P_{reactant} \text{ and } \Delta^{\neq} \text{ is large}$$

Then the reaction rate in solution would be low than ideal solution rate.

Case (iii)

When $P_{solvent} \approx P_{activated\ complex}$, has much different from that of reactant than the RT Ln K_s/K_o will be positive value and make the reaction rate in solution high, that is RT Ln K_s is large.

Thus the kinetic study of solution is very complicated but in general,

NOTE

(i) If the product of the reaction is polar, then the reaction is favoured in polar solvent.

(ii) If the product of the reaction is nonpolar, then the reaction is favoured in non-polar solvent.

(iii) If the product of the reaction having high internal pressure then the reaction is favoured in solvent having high internal pressure.

13.5 EFFECT OF SOLVENT

It can be classified in the following topics

13.5.1 REACTION BETWEEN IONS

The electrostatic forces between ions are much stronger than non electrostatic, forces. The pre exponential factors of ionic reactions depend in simple electrostatic principle. If ions are oppositely charged the pre exponential factors are abnormally high, where as if the charges are the same they are abnormally low.

The reaction between ions in solution has markedly affected by solvent and its dielectric constant. In order to explain this effect there are two models into account.

(i) Single sphere model

(ii) Double sphere model

Single sphere model

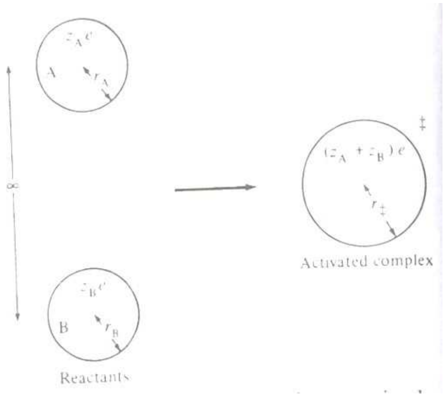
Here slightly different relationship has been obtained from that of double sphere model.

a) The reacting ions are regarded as becoming merged into one single sphere which has charge equal to the algebric sum of the both the ions.

b) The rate equation for this model is derived by Born.

c) Consider the process of charging a conducting sphere of radius "r" from an initial charge if zero to a final charge Z_e.

(d) This process is carried out by transporting from infinite distance to small increment of charge equal to edλ.



λ = Parameter which varies from zero to ‘z’.

At any time the charge of the sphere has written as λe, and if at a given instant the increment of charge is at a distance x from the ion the force acting on it is

$$f = \frac{e\lambda}{4\pi\varepsilon_o \varepsilon x^2}$$

$$df = \frac{\lambda e.ed\lambda}{4\pi\varepsilon_o \varepsilon x^2} = \frac{\lambda e^2 d\lambda}{4\pi\varepsilon_o \varepsilon x^2} \rightarrow (1)$$

The work of moving the increment from x to dx is

$$dw = \frac{\lambda e^2 d\lambda dx}{4\pi\varepsilon_o \varepsilon x^2}$$

The total work of charging is obtained by carried out by double integration

$$\lambda_{0\rightarrow Z}, \qquad x_{\alpha\rightarrow r}$$

$$\int dw = \frac{-e^2}{4\pi\varepsilon_o\varepsilon}\int_0^z \int_\alpha^\gamma \lambda d\lambda \frac{dx}{x^2} \quad , \quad = -\frac{e^2}{4\pi\varepsilon_o\varepsilon}\int_0^Z \lambda d\lambda \left[-\frac{1}{x}\right]_\alpha^\gamma$$

$$= -\frac{e^2}{4\pi\varepsilon_o\varepsilon}\left(-\frac{1}{r}\right)\left[\frac{\lambda^2}{2}\right]_0^Z \quad , \quad w = \frac{e^2 Z^2}{8\pi\varepsilon_o\varepsilon r} \text{ ------- } (3)$$

$$G^0_{es(B)} = \frac{Z_B^2 e^2}{8\pi\varepsilon_o\varepsilon r_B} \qquad G^{0\neq}_{es} = \frac{(Z_A + Z_B)^2 e^2}{4\pi\varepsilon_o\varepsilon r^{\neq}}$$

The charge in electrostatic ΔG^{0}_{es} is

$$\Delta G^{0\neq}_{es} = \frac{e^2}{8\pi\varepsilon_o\varepsilon}\left(\frac{(Z_A+Z_B)^2}{\gamma^{\neq}} - \frac{Z^2_A}{\gamma_A} - \frac{Z^2_B}{\gamma_B}\right) \rightarrow (4)$$

Free energy per molecule is

$$\Delta G^{0\neq}_{es} = \frac{Ne^2}{8\pi\varepsilon_o\varepsilon}\left(\frac{(Z_A+Z_B)^2}{\gamma^{\neq}} - \frac{Z^2_A}{\gamma_A} - \frac{Z^2_B}{\gamma_B}\right) \rightarrow (5)$$

$$\Delta G^{\neq}_{es} = \Delta G^{\neq}_{es} + \Delta G^{\neq}_{nes}.$$

$G^{0\neq}_{es}$ = Electrostatic contribution to the Gibbs energy of activation

$G^{0\neq}_{nes}$ = Non-Electrostatic contribution to the Gibbs energy of activation

Substitute equation (5) in ARRT equation

$$K = \frac{KT}{h} e^{-\Delta G^{o\neq}/RT\, r}$$

$$K_r = \frac{RT}{Nh} e^{\frac{Ne^2}{8\pi\varepsilon_o\varepsilon RT}\left(\frac{(Z_A+Z_B)^2}{\gamma^{\neq}} - \frac{Z^2_A}{\gamma_A} - \frac{Z^2_B}{\gamma_B}\right)} . e^{-\frac{\Delta G_{nes}}{RT}} \rightarrow (6)$$

Taking natural logarithms we obtain

$$\ln k_r = \ln \frac{RT}{2h} . e^{\frac{-\Delta G^{\neq}nes}{RT}} - \frac{e^2}{8\pi\varepsilon_o\varepsilon RT}\left(\frac{(Z_A+Z_B)^2}{\gamma^{\neq}} - \frac{Z^2_A}{\gamma_A} - \frac{Z^2_B}{\gamma_B}\right) \rightarrow (7)$$

This may be written as

$$\ln k_r = \ln k_0 - \frac{e^2}{8\pi\varepsilon_o\varepsilon RT}\left(\frac{Z_A^2 + Z_B^2 + 2Z_A Z_B}{\gamma^{\neq}} - \frac{Z_A^2}{\gamma_A} - \frac{Z_B^2}{\gamma_B}\right) \rightarrow (8),$$

when $\gamma^{\neq} = \gamma_A = \gamma_B$

The equation becomes double sphere model

Double sphere model

According to ARRT, general reaction is as follows

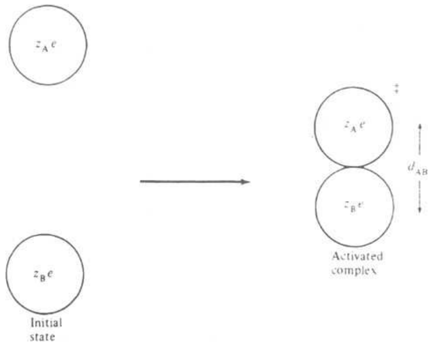
Ions ↔ A.C →product

$$k_r = k^{\neq}\frac{RT}{Nh}, \quad \Delta G^{\neq} = -RT\ln k^{\neq}, \quad k^{\neq} = e^{-\frac{\Delta G^{\neq}}{RT}}$$

Thus $k_r = \frac{RT}{Nh}e^{-\frac{\Delta G^{\neq}}{RT}}$ -------- (1)

It is a thermodynamic statement of ARRT

The charged ions in solution are considered to be conducting sphere and solvent regarded as fixed dielectric constant and hence the spheres are hard and rigid



γ_A and γ_B = Radius of two ions, $Z_A e$ and $Z_B e$ = the charges on the ions

e = 1.602x10^{-19} C.

Initially the ions are infinite distance apart. In this particular model known as double sphere model (hence no force between them)

When the ions are separated by a distance ‘x’ the force acting between them is

according to coulombs law

$$f = \frac{Z_A Z_B e^2}{4\pi\varepsilon_o \varepsilon x^2} \text{ ------- (2)}$$

Work done in moving two ions together to a distance dx is given by

$dw = -\frac{Z_A Z_B e^2}{4\pi\varepsilon_o \varepsilon x^2}dx$, ‘-ve’ sign implies the decrease of ‘x’.

The work done on the system in moving the ions from $x = \alpha$ to $x = d_{AB}$

$$\int dw = -\int_{\alpha}^{d_{AB}} \frac{Z_A Z_B e^2}{x^2 4\pi\varepsilon_o \varepsilon}dx \quad , \quad w = -\frac{Z_A Z_B e^2}{4\pi\varepsilon_o \varepsilon}\int_{\alpha}^{d_{AB}} \frac{1}{x^2}dx$$

$$w = -\frac{Z_A Z_B e^2}{4\pi\varepsilon_o\varepsilon}\left[-\frac{1}{x}\right]_{\alpha}^{d_{AB}} \qquad w = \frac{Z_A Z_B e^2}{4\pi\varepsilon_o\varepsilon d_{AB}} \quad \text{-------} \quad (3)$$

NOTE

This work is +ve when the ions are same sign. This is –ve if opposite charge. Hence the work is electrostatic contribution to the Gibbs free energy of activation.

$$\frac{\Delta G^{\neq}}{N} = \frac{Z_A Z_B e^2}{4\pi\varepsilon_o\varepsilon d_{AB}}(electrostatic) + \frac{\Delta G_{nes}^{\neq}}{N}\ (nonelectrostatic)$$

$$\Delta G^{\neq} = \frac{N Z_A Z_B e^2}{4\pi\varepsilon_o\varepsilon d_{AB}} + \Delta G_{nes}^{\neq} \quad \text{---------} \ (4)$$

Substitute in equation (1)

$$k_r = \frac{RT}{Nh} e^{-\frac{\Delta G^{\neq}}{RT}}, \qquad k_r = \frac{RT}{Nh} e^{-\frac{Z_A Z_B e^2 N}{RT . d_{AB} 4\pi\varepsilon_o\varepsilon}} . e^{-\frac{\Delta G_{nes}}{RT}}$$

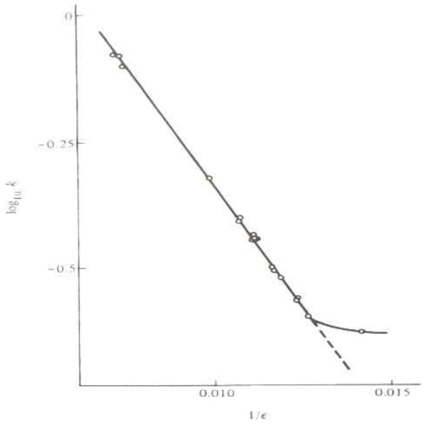
$$\ln k_r = \ln\left(\frac{RT}{Nh} . e^{-\frac{\Delta G_{nes}}{RT}} . e^{-\frac{Z_A Z_B e^2 N}{RT . d_{AB} 4\pi\varepsilon_o\varepsilon}}\right)$$

$$\ln k_r = \ln \frac{RT}{Nh} e^{-\frac{\Delta G^{\neq}_{nes}}{RT}} - \frac{Z_A Z_B e^2 N}{4\pi\varepsilon_o\varepsilon d_{AB} RT} \quad \text{--------} \ (5)$$

$$\ln\frac{k_r}{k_0} = -\frac{Z_A Z_B e^2 N}{4\pi\varepsilon_o\varepsilon d_{AB} RT}$$

K_0 = rate constant of reaction in solvent of infinite dielectric constant. Plot of k_r vs 1/ε will give straight line. It is experimentally verified but there is a deviation in low dielectric constant. From the slope the d_{AB} can be calculated, it has the the value of few hundred picometer (10^{-12}).

NOTE



13.5.2 ION-DIPOLE REACTION

Ion-dipole

In reality, many ions have a distribution of charges, and this makes a difference to the electrostatic interactions. Much interest is between ion and dipole molecules or between two dipole molecules.

The electrostatic free energy contribution is from single sphere model

Sphere of radius – r

Net charge - Z_e

Dipole moment –μ

$$\Delta G^{o}_{es} = \frac{z^2e^2}{8\pi\varepsilon_o\varepsilon r} + \frac{3\mu^2}{16\pi\varepsilon_o\varepsilon r^3} \rightarrow (1)$$

For a bimolecular reaction

$$A + B \rightarrow X^{\neq} \rightarrow product$$

$$\Delta G^{o}_{es}(A) = \frac{z_A^2e^2}{8\pi\varepsilon_o\varepsilon r_A} + \frac{3\mu_A^2}{16\pi\varepsilon_o\varepsilon r_A^3} \rightarrow (2)$$

$$\Delta G^{o}_{es}(B) = \frac{z_B^2e^2}{8\pi\varepsilon_o\varepsilon r_B} + \frac{3\mu_B^2}{16\pi\varepsilon_o\varepsilon r_B^3} \rightarrow (3)$$

$$\Delta G^{o}_{es}(\neq) = \frac{(z_A+z_B)^2e^2}{8\pi\varepsilon_o\varepsilon r_{\neq}} + \frac{3\mu_{\neq}^2}{16\pi\varepsilon_o\varepsilon r_{\neq}^3} \rightarrow (4)$$

So the electrostatic contribution for activation

$$\Delta G^{o\neq}_{es} = \frac{e^2}{8\pi\varepsilon_o\varepsilon}\left(\frac{(z_A+z_B)^2}{r_{\neq}} - \frac{z_A^2}{r_A} - \frac{z_B^2}{r_B}\right) + \frac{3}{16\pi\varepsilon_o\varepsilon}\left(\frac{\mu_{\neq}^2}{r_{\neq}^3} - \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^3}\right) \rightarrow (5)$$

The non electrostatic contribution say $\Delta G^{\neq}_{nes}$

$$\Delta G^{\neq} = \Delta G^{\neq}_{es} + \Delta G^{\neq}_{nes}$$

From ARRT

$$\ln k = \ln k_o - \frac{e^2}{8\pi\varepsilon_o KT\varepsilon}\left(\frac{(z_A + z_B)^2}{r_{\neq}} - \frac{z_A^2}{r_A} + \frac{z_B^2}{r_B}\right) \frac{3}{16\pi\varepsilon_o KT\varepsilon}\left(\frac{\mu_{\neq}^2}{r_{\neq}^3} - \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^3}\right) \rightarrow (6)$$

Assume radii do not vary as much as the charge and dipole moments, it is a useful approximation to treat them all the same and equal to d_{AB}.

$$\gamma_A = \gamma_B = \gamma_{\neq} = d_{AB}$$

Then equation (6) becomes

$$\ln k = \ln K_o - \frac{z_A z_B e^2}{4\pi\varepsilon_o \varepsilon d_{AB} KT} - \frac{\mu_{\neq}^2 - \mu_A^2 - \mu_B^2}{16\pi\varepsilon_o \varepsilon d_{AB}^3 KT} \rightarrow (7)$$

If both the species are charged the second term in equation (6) or equation (7) is usually much greater than the third.

If either reactant has no charge, however, the final term becomes predominant.

If the reacting species are uncharged, converted into activated complex has more polar than reactant ($\gamma_{\neq}$ is large compared to γ_A and γ_B, the rate constant increases with increasing dielectric constant.

$$\Delta\mu_o^2 \equiv \frac{\mu_{\neq}^2 - \mu_A^2 - \mu_B^2}{\left(1.602\times10^{-29} Cm\right)^2} \rightarrow (8)$$

1.602×10^{-29} Cm is the dipole moment of two elementary charges (1.602×10^{-19}C) separated by a distance 10^{-10}m.

13.6 EFFECT OF SUBSTITUENTS ON REACTION RATES

How the rate of the reaction or equilibrium constant will affect by substitution in either m or p was explained by Hammet. It is a linear relationship between Gibbs free energy of any two set of reactions.

13.6.1 HAMMETT'S EQUATION

According to Hammetts relationship the rate constant for the reaction of one compound is related to that for the unsubstituted parent compound in terms of two parameters ρ and σ

For rate constants the relationship is

$$\log\frac{k}{k_0} = \rho\sigma$$

σ - Substituent constant is a number (+ve of –ve)

+ve = for electron withdrawing substituent.

-ve = for electron releasing substituent.

ρ - reaction constant is n number due to external condition, solvent etc.

ρ is +ve if solvent will assist the electron withdrawing nature or releasing nature.

ρ is –ve if solvent will against the electron withdrawing or releasing nature.

$$C_6H_5COOH \leftrightarrow C_6H_5COO^- + H^+ \quad \rho = 1 \text{ (constant)}$$

$$NO_2\text{-}C_6H_5COOH \leftrightarrow NO_2\text{-}C_6H_5COO^- + H^+ \quad \sigma_m = 0.710$$

$$\log\frac{k}{k_0} = \rho\sigma_m = 0.710 \times 1$$

$$\log\frac{k}{k_0} = 0.710$$

$$\log k = \log k_0 + 0.710$$

$$\frac{k}{k_0} = \log^{-1} 0.710$$

$$\frac{k}{k_0} = 5.31$$

$$k = k_0\, 5.31$$

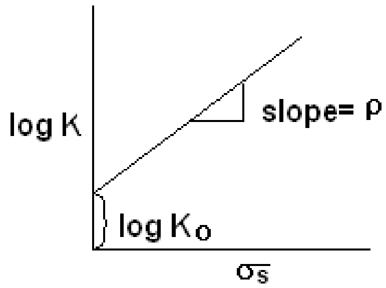
ie. Rate of ionization of substituted benzoic acid is 5.31 times greater than unsubstituted benzoic acid.

Using the same value of ρ and σ for hydrolysis of benzamide in 60% ethanol at 80°. We can calculate the m-nitrobenzamide which can be hydrolysed 0.615 times as fast as benzamide.

NOTE

$$\log k = \log k_0 + \rho\sigma_s$$

When we plot log k vs σ_s is a linear relation, from that we can calculate the value of ρ.



Linear free energy relation of Hammet equation:

The rate constant of a reaction related with free energy of activation by.

$$k = \frac{K_B T}{h} e^{-\frac{\Delta G^{\neq}_0}{RT}} \text{ ------- (1)}$$

$$k_{eq} = e^{-\frac{\Delta G^{\neq}_0}{RT}} \text{ -------- (2)}$$

Taking log for equation (1)

$$\log k = \log \frac{k_B T}{h} - \frac{\Delta G^{\neq}_0}{2.303RT}$$

Hammett equation

$$\log k = \log k_0 + \rho\sigma \quad (4)$$

Substitute (3) in (4)

$$\log k_B \frac{T}{h} - \frac{\Delta G^{\neq}}{2.303RT} = \log k_B \frac{T}{h} - \frac{\Delta G_o^{\neq}}{2.303RT} + \rho\sigma$$

$$\frac{\Delta G^{\neq}}{2.303RT} = \frac{\Delta G_o^{\neq}}{2.303RT} - \rho\sigma \times 2.303RT$$

$$\Delta G^{\neq} = \Delta G_0^{\neq} - 2.303RT\rho\sigma \quad (5)$$

$\Delta G^{\neq}$ = free energy of activation for substituted compound

NOTE

$\Delta G^{\neq o}$ = free energy of activation for parent compound

Equation (5) with a particular value of ρ, applies to any reaction involving a reactant having series of substituents.

For another series has different ρ value and by assuming σ is constant.

$$\Delta G^{\neq'} = \Delta G_0^{\neq'} - 2.303RT\rho'\sigma$$

$$\frac{\Delta G^{\neq}}{\rho'} = \frac{\Delta G_0^{\neq}}{\rho'} - 2.303RT\sigma \quad \text{------- (6)}$$

Equation (5) may be written as

$$\frac{\Delta G^{\neq}}{\rho} = \frac{\Delta G_0^{\neq}}{\rho} - 2.303RT\sigma \quad \text{------ (7)}$$

Subracting (7) – (6)

$$\frac{\Delta G_0^{\neq}}{\rho} = \frac{\Delta G_0^{\neq'}}{\rho'}$$

$$\Delta G_0^{\neq} - \frac{\rho}{\rho'}\Delta G_0^{\neq'} = constant.$$

Then there is a linear relationship between Gibbs energy of activation with in any two set of homogeneous reaction.

13.6.2 TAFT EQUATION

When Hammet plot of log K/K_o against σ are extended to the reactions of aliphatic compounds and to those of o-substituted benzene derivatives the straight line no longer result. Thus Taft derived another equation, including polar factor, conjugation factor and steric effect hence used for aliphatic compound also.

$$\log K/K_o = P + C + S$$

P – polar factor

C – Conjugation factor

S – Steric effect.

He studied acid hydrolysis of ester as well as base hydrolysis of ester, single equation is not hold good for both the case. The polar effect has neglected in acid hydrolysis,

NOTE

$$\log (K/K_o)_{base} = P + C + S$$

$$\log (K/K_o)_{acid} = C + S$$

$$\log (K/K_o)_{base} = P + \log (K/K_o)_{acid}$$

$$\boxed{\log (K/K_o)_{base} - \log (K/K_o)_{acid} = P = P^* \sigma^*}$$

This equation is known as Taft Equation.

13.7 Check Your Progress

1. What is the difference between the primary and secondary salt ?
2. What is the effect of ionic strength on the rate of reaction?

13.8 Answers to check your progress questions

1. Primary salt effect. It has been observed that the rate of a reaction can be altered by the presence of non-reacting or inert ionic species in the solution. This effect is profound when the reaction takes place between ions, even at low concentrations.
The term “secondary kinetic salt effect" is used to indicate a kinetic. salt effect due to a change in concentration of the reacting molecules on. account of a change in the inter-ionic forces.1,2. Such effects are very commonly met in the study of kinetic reactions.

2.This question might be simple for those who might have understood the concept of CHEMICAL KINETICS in which there’s a beautiful equation given to us with which we can find out rate of reaction in addition to this entropy also changesi.e with increase in IONIC strength of a compound the chemical reaction rate **decreases.**some factors affecting the reaction rates might also be included such a s temperature,pressure and concentration mainly

13.9 Summary

- ✓ In this module, focus was laid on primary salt effect and secondary salt effect.
- ✓ It has been observed that the rate of a reaction can be altered by the presence of non-reacting or inert ionic species in the solution. This effect is profound when the reaction takes place between ions, even at low concentrations. This influence of charged species on the rate of the reaction is referred to as salt effect.
- ✓ The salt effect is classified as Primary salt effect and Secondary salt effect.
- ✓ The primary salt effect takes into account the influence of electrolyte concentration on the activity coefficient and hence the rate of the reaction.

NOTE

✓ The secondary salt effect is the actual change in the concentration of the reacting ions resulting from the addition of electrolytes

13.10 Keywords

Primary salt effect- It has been observed that the rate of a reaction can be altered by the presence of non-reacting or inert ionic species in the solution. This effect is profound when the reaction takes place between ions, even at low concentrations.

The secondary salt effect- It is the actual change in the concentration of the reacting ions. resulting from the addition of electrolytes.

13.11 Self-assessment questions and exercises

1. Explain in detail about effect of solvent with example.
2. Explain the dielectric constant.
3. What is meant by Hammett and Taft equations?

13.12 Further readings

1. Mendham, J.; Denney, R. C.; Barnes, J. D.; Thomas, M. J. K. (2000), Vogel's Quantitative Chemical Analysis (6th ed.), New York: Prentice Hall, p. 28, *ISBN 0-582-22628-7*

2. **Physical chemistry**, Peter Atkins, Julio De Paula, 9th edition,

Unit-14: ACID BASE CATALYSIS

Structure

NOTE

14.0 Introduction

The acid catalysis and base catalysis, a chemical reaction is catalyzed by an acid or a base. By Brønsted–Lowry acid–base theory, the acid is the proton (hydrogen ion, H^+) donor and the base is the proton acceptor. Typical reactions catalyzed by proton transfer are esterification's and aldol reactions. In these reactions, the conjugate acid of the carbonyl group is a better electrophile than the neutral carbonyl group itself. Depending on the chemical species that act as the acid or base, catalytic mechanisms can be classified as either specific catalysis and general catalysis. Many enzymes operate by specific catalysis.

14.1 Objectives

After going through this unit, you will be able to:

- Understand about the Acid and base catalysts.
- Understand the methods of determining the Enzyme catalysis
- Explain the concept of effect of pH and temperature on enzyme catalyzed reactions

14.2 ACID BASE

A reaction is catalysed by H^+ or H_3O^+ ion is said to be specific acid catalysis reaction. Some reaction is catalysed by

NOTE

any Bronsted acid is said to be general acid catalysis reaction. If a reaction is catalysed by OH- ion is specific, base catalysis or by any base are said to be general base catalysis reaction Some reaction catalysed by both acid and base are said to be acid-base catalysis.

If a reaction is carried in aqueous acid the rate

$$r = K_o[S] + K_H[S][H^+] \rightarrow (1)$$

If OH^- also included

$$r = K_o[S] + K_H[S][H^+] + K_{OH}[S][OH^-] \rightarrow (2)$$

Divide through out by [S]

$$K = K_o + K_H[H^+] + K_{OH}[OH^-] \rightarrow (3)$$

Note:

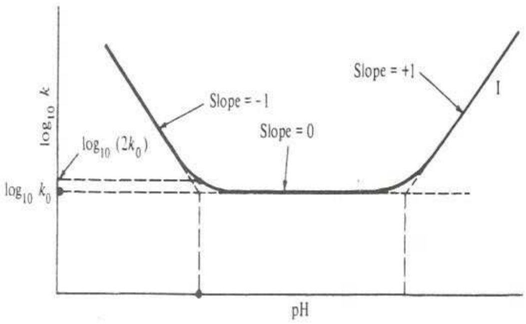
$$r = K[S]$$

$$\frac{r}{[S]} = K$$

Skrabal diagram:

The plot of log K vs pH of the solution is known as Skrabal diagram.

For mutarotation of Glucose



CASE I

For acid catalyzed reaction:

$$K = K_{H^+}[H^+]$$

$$LogK = LogK_{H^+} + Log[H^+]$$

$$LogK = LogK_{H^+} - pH$$

NOTE

CASE II

$$K = K_{OH^-}\left[OH^-\right]$$

$$LogK = LogK_{OH^-} + Log\left[OH^-\right]$$

$$LogK = LogK_{OH^-} + Log\frac{K_w}{H^+}$$

$$LogK = LogK_{OH^-} K_w + pH$$

CASE III

The horizontal line with zero slope corresponds to uncatalysed reaction. Zero order with respect to acid/base

14.3 ACIDITY FUNCTIONS

The first acidity function proposed, other than the pH, is due to Hammett and Doyrup, is based on equilibrium of the type

$$B + H^+ \leftrightarrow BH^+$$

Eg: $C_6H_5NH_2 + H^+ \leftrightarrow C_6H_5NH_3^+$

Equilibrium constant for such reactions is

$$K = \frac{\left[BH^+\right]}{[B][H^+]} \times \frac{Y_{BH^+}}{Y_B.Y_{H^+}} \text{ ------- (1)}$$

Where the Y's are the activity co- efficient. Where B, $[BH^+]$ can be distinguished

Spectrophotometrically, it is possible to measure $\frac{[BH^+]}{[B]}$, and K also can be measured in dilute solutions.

Taking log in Equation (1)

$$\log k = \log\frac{[BH^+]}{[B][H^+]} + \log\frac{Y_{BH^+}}{Y_BY_{H^+}}$$

$$\log k - \log\frac{[BH^+]}{[B]} = \log[H^+] - \log Y_{H^+} + \log\frac{Y_{BH^+}}{Y_B}$$

$$\log k - \log\frac{[BH^+]}{[B]} = -\log a_{[H^+]} - \log\frac{Y_B}{Y_{BH^+}}$$

$$\log k - \log \frac{[BH^+]}{[B]} = -\log a_{[H^+]} \cdot \frac{Y_B}{Y_{BH^+}}$$

$$Y_{H^+}.[H^+] = a_{H^+}$$

Left hand side of equation can be measured by experimental way. The function on the right hand side can be measured in acidic solution by introducing a suitable indicator and measuring the concentrations of the two species. The quantity on the right-hand side.

$$H_O = -\log_{10}\left(a_{H^+} \frac{Y_B}{Y_{BH^+}} \right)$$ Hammett acidity function

$$S + H^+ \leftrightarrow SH^+ (rapid) \rightarrow [SH^+]^{\neq}$$

$$SH^+ \rightarrow product(slow)$$

If the second step is slow and rate controlling step, the overall rate is proportional to the ion concentration of activated complex $[(SH^+)]^{\neq}$

$$\gamma = k^{\neq}[SH^+]^{\neq}$$

$$K_s^{\neq} = \frac{[SH^+]^{\neq}}{[SH^+]} \frac{Y^{\neq}}{Y_{SH^+}} \text{ -------- (1)}$$

$$K_s^{\neq} = \frac{a^{\neq}_{SH^+}}{a_{SH^+}}; \qquad [SH^+]^{\neq} = \frac{K_S^{\neq}[SH^+]Y_{SH^+}}{Y^{\neq}} \text{ -------- (2)}$$

$a^{\neq}$ and $Y_{\neq}$ are activity coefficient.

For the pre equilibrium, $$k_s = \frac{a_{SH^+}}{a_s a_H} = \frac{[SH^+]\, Y_{SH^+}}{[S]\, Y_S a_{H^+}} \text{ ------- (3)}$$

From equation (2) $\gamma = k^{\neq}[SH^+]^{\neq}$

$$rate = \frac{k^{\neq} k_s^{\neq}[SH^+]Y_{SH^+}}{Y^{\neq}}$$

From equation (3) $$k_s = \frac{[SH^+]\, Y_{SH^+}}{[S]\, Y_S a_{H^+}}$$

14.4 BRONSTED RELATIONS

Since catalysis by acids and bases usually involves the transfer of proton from or to the catalyst, it is natural to seek a correlation between the effectiveness of catalyst and its

strength as an acid or base. The most satisfactory relationship was given by Bronsted termed as Bronsted relations,

(i) The catalytic constant is related with dissociation constant K_a by,

$$k_a = G_a K_a^{\alpha}$$

Where, G_a and α are constan, k_a catalytic constant, K_a Dissociation constant, α always less than unity.

(ii) Similarly, for a base catalysis

$$k_b = G_b K_b^{\beta}$$

$$G_b' = \left(\frac{1}{K_a}\right)^{\beta} \qquad K_b = \frac{1}{K_a}$$

where k_b is the dissociation constant for the base; k_a that for its conjugate acid; β is a constant that is again less than unity.

Modification of above equation:

If we applied this relation to an acid catalysis reaction of dibasic nature i.e. acid has more than one ionizable proton or base more than one centre to accept proton, the modification should be made.

$CH_3(CH_2)COOH$ – Long chain fatty acids

$HOOC\text{-}CH_2(CH_2)_nCOOH$ – Dibasic acid

(i) In the dibasic acid there is negligible interaction between the two carboxyl groups. The dissociation constant of the dicarboxylic acid is twice that of the monocarboxylic acid. Since the ion can be formed by loss of either of two proton. For the same reason the catalytic activity or catalytic constant for dibasic acid is twice that of monobasic acid.

Since the ratio of 2 in the acid strengths leads to the ratio of 2^{α} in the catalytic constant and this is generally less than 2. This anomaly is avoided if both the acid strengths and catalytic constant are divided by the number of proton involved in the dissociation.

(ii) In the case of the two acids $HOOC(CH_2)_nCOOH$ and $HOOC(CH_2)_nCOO^-$, both of which have one dissociable proton, the catalytic strength are the same. On the other hand, the acid strength of second is one half of first since the ion $^-OOC(CH_2)_nCOO^-$ in which the second dissociates has two points at which a proton may be added, where as the ion of the first acid has only one site. To remove the inconvenience it is necessary to multiply the dissociation constant of $HOOC(CH_2)COO^-$ by 2 before inserting it into the equation

$$\frac{k_a}{P} = G_a \left(\frac{qK_a}{P} \right)^{\alpha}$$

$$\frac{k_a}{q} = G_b' \left(\frac{P}{qK_a} \right)^{\beta}$$

ρ – number of dissociable proton bound equally strongly in the acid, while q is the number of equivalent positions in the conjugate base to which a proton may be attached.

The Bronsted relationships are special cases of the linear Gibbs energy relationship.

$$\log k = \log K_o + \delta\rho$$

$$\log k = \log K_o + \delta\rho'$$

δ is same in both the cases but the reaction constant ρ and ρ' are different in equilibrium and rate constant equations.

$$\frac{1}{\rho} \log k = \frac{1}{\rho} \log k_o + \delta$$

and $$\frac{1}{\rho'} \log k = \frac{1}{\rho'} \log k_o + \delta$$

Subtraction leads to $\frac{1}{\rho} \log k - \frac{1}{\rho'} \log k = \text{constant}$

And therefore $$\log \frac{k^{\frac{1}{\rho}}}{K^{\frac{1}{\rho'}}} = cons\tan t$$

NOTE

NOTE

This may written as $\log \frac{k}{K^{\rho}} = constant$

or k = GK_o

14.5 ZUCKER- HAMMETT HYPOTHESIS

The acidity function is used to check the existence of correlation between H_o and rate constant, a pre-equilibrium of the type as give below can be established.

$X + H^+ \overset{K}{\longleftrightarrow} XH^+ (fast)$ $XH^+ \rightarrow P$ (slow)

The second step is slow and rate determining step.

The activated complex has equilibrium with further activated complex.

$$XH^+ \overset{K^1}{\longleftrightarrow} [XH^+]^{\neq} \overset{K_2}{\longrightarrow} P$$

$$rate = k_2 [XH^+]^{\neq} \text{ ------- (1)}$$

$$K_{eq} = \frac{[XH^+]\gamma^{\neq}}{[XH^+]\gamma_{XH^+}} = \frac{a^{\neq}}{a_{XH^+}} \text{ ------- (2)}$$

From (2) $[XH^+]^{\neq} = \frac{K^1_{eq}[XH^+]\gamma_{XH^+}}{\gamma^{\neq}}$ -------- (3)

(3) in (1) $rate = \frac{k_2 k^1_{eq}[XH^+]\gamma_{XH^+}}{\gamma^{\neq}}$ -------- (4)

From the pre equilibrium $k_{eq} = \frac{[XH^+]\gamma_{XH^+}}{[X][H^+]\gamma_{H^+}\gamma_X}$

$$[XH^+] = \frac{\gamma_X [X] a_{H^+} K_{eq}}{\gamma_{XH^+}} \text{ ------- (5)}$$

Substitute (5) in (4) $\gamma = \frac{k_2 k'_{eq} k_{eq} \gamma_X [X] a_{H^+} \gamma_{XH^+}}{\gamma^{\neq} \gamma_{XH^+}}$

$$\gamma = \frac{k_2 k'_{eq} k_{eq} \gamma_X a_{H^+}}{\gamma^{\neq}} [X]$$

For a first order rate, k= r /[s]

NOTE

$$k = \frac{k_2 k'_{eq} k_{eq} \gamma_X a_{H^+}}{\gamma^{\neq}}$$

[S] = [X]

Taking natural logarithm for the above

$$\log k = \log k_2 k'_{eq} k_{eq} + \log \frac{\gamma_X a_{H^+}}{\gamma^{\neq}} \quad \text{---------(6)}$$

$$\log k = \log k_2 k'_{eq} k_{eq} - H_0 \quad \text{--------- (7)}$$

H_0 is acidity function. The equation shows that a correlation will exist between log k and H_0, reaction mechanism involving pre-equilibrium.This same mechanism tentatively modified by 'Zucker' by including water (solvent) in the slow process as follows

$$X + H^+ \overset{K}{\leftrightarrow} XH^+ \overset{K'}{\leftrightarrow} [XH^+]^{\neq} \rightarrow product \quad \text{Slow/}H_2O$$

follow the derivation equation (6) becomes,

$$\log k = \log k_2 k'_{eq} k_{eq} + \log \frac{\gamma_X a_{H^+} a_{H_2O}}{\gamma^{\neq}}$$

The suggestion was that it might be possible to decide between the two mechanism by seeing whether the rate constant showed better correlation with p^H or with $H_{0.}$ Unfortunately this Hammett-Zucker hypothesis did not prove reliable.

14.6 ENZYME CATALYSIS

Enzymes are proteins with high molecular mass of order 10000 or even more they are derived from living organism.

Enzyme catalysed reactions are specific in nature.

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2EtOH + 2CO_2$$

$$urea \xrightarrow{urease} 2NH_3 + CO_2$$

Mechanism and kinetics of enzyme catalysed reaction

$$E + S \underset{K_{-1}}{\overset{K_1}{\longleftrightarrow}} ES$$

$$[ES] \xrightarrow{K_2} P + S$$

E= enzyme, s =substrate

NOTE

Apply steady state approximation for [ES].

$$K_1[E][S]-K_{-1}[ES]-K_2[ES]=0\text{----------}(1)$$

$$[ES]K_{-1}+K_2=K_1[E][S]$$

$$[ES]=\frac{K_1[E][S]}{K_{-1}+K_2}\rightarrow(2)$$

$$[E] = [E_0]-[ES]$$

[E]=Equilibrium constant

Substitute in equation, $K_1[S][(E_0)-(ES)]=K_{-1}[ES]-K_2[ES]$

$$[ES]=\frac{K_1[S][E_0]}{K_{-1}+K_2+K_1[S]}$$ Rate of the reaction $r=k_2[ES]$

$$r=\frac{K_2K_1[S][E_0]}{K_1[S]+K_{-1}+K_2}\rightarrow(3)$$ Divide the equation (3) by k_1

$$r=\frac{K_2[E_0][S]}{[S]+K^{-1}+\frac{K_2}{K_1}}$$

$$r=\frac{K_2[E_0][S]}{[S]+K_m}\text{--------}(5)$$

where km = $k_{-1}+k_2/k_1$ --- Michaelis constant. This rate equation is known as Michaelis –Menton equation.

At very high concentration of substrate the rate will be maximum.

From equation (5) km<<[S]

$$r=\frac{k_2[E_0][S]}{[S]+K_m}\quad,\quad r_{max}=\frac{k_2[E_0][S]}{[S]}$$

$$r_{max}=k_2[E_0]\text{-------}(6)$$

Substitute (6) in (5)

$$r=\frac{k_2[E_0][S]}{[S]+K_m}=\frac{\gamma_{max}[S]}{[S]+K_m}\text{-------}(7)$$

Limiting cases:

Case (i)

NOTE

When km >> [s]

$$r = \frac{\gamma_{\max}[S]}{K_m} = k'[s]$$

Reaction is first order with respect to [s].

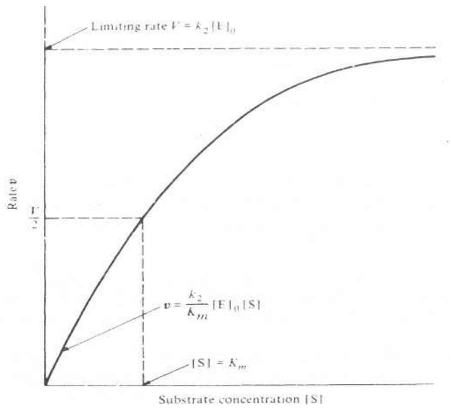
Case (ii)

[s]>>km, $r = \frac{\gamma_{\max}[s]}{[s]} = \gamma_{\max} = cons\tan t$

Case (iii)

If s = k_m, $r = \frac{\gamma_{\max}[s]}{2[s]} = \frac{1}{2}\gamma_{\max}$

When we plot a graph K_m is defined as concentration of substrate at which the rate of formation of product is half the maximum rate at high concentration of substrate.



Why the rate of enzyme catalyst reaction changes from first order to zero order as the concentration of [s] increases?

Each enzyme molecule has one or more active sites at which the substrate must be adsorbed in order that catalytic action must occur.

At low [s]

As the [s] increases the number of sites which are occupied increases and the rate also increases.

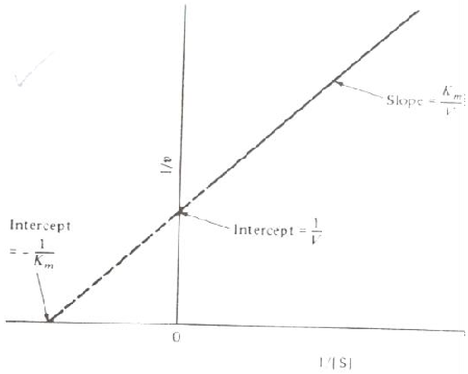
At high [s]

NOTE

All the active sites are already occupied and the further increase in [s] can not further increase in rate and become zero order. It is very difficult to determine the γ_{max} and K_m from the plot γ vs [S].

(i) Line Weaver-Burk Method:

$$r = \frac{\gamma_{max}[S]}{[S]+K_m}$$



$$\frac{1}{r} = \frac{[S]+K_m}{\gamma_{max}[S]}$$

$$\frac{1}{r} = \frac{1}{\gamma_{max}} + \frac{k_m}{\gamma_{max}[s]}$$ Plot between 1/r vs 1/[s]

14.7 EFFECT OF pH AND TEMPERATURE ON ENZYME CATALYZED REACTIONS

Influence of pH

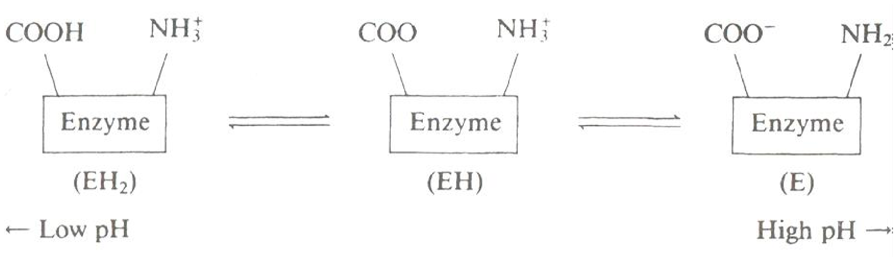
The pH of the solution usually has a very marked effect on the rate of an enzyme reaction. In most cases the rates of enzyme reaction passes through a maximum as the pH is varied. The pH corresponding to the maximum rate is known as optimum pH. Its value varies with the nature of substrate and with the substrate concentration.

Effects of pH are irreversible if the acidity or basicity become too high, since the ternary substance of the protein is destroyed. Reversible pH changes occur when the pH is not taken too far from the pH optimum.

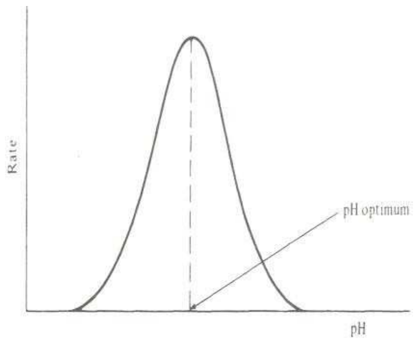
With in a certain pH range the pH can be changed back and forth without any permanent affects ensuring.

This behaviour was first explained by Michaelis to postulate at least two ionizing groups as playing an important role at the active centre, these groups are $–NH3^+$ and –COOH, the ionization at

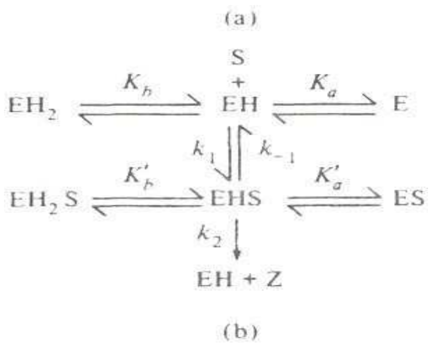
active centre may be represented as



The pH behaviour can be explained by postulating that the intermediate, Zwitter ion, form is enzymatically active, but that the species to left and right are inactive. The concentration of intermediate goes through a maximum as the pH is varied so that the rate passes through a maximum.



Mechanism:



Applying steady state approximation for the above mechanism .

At low substrate concentration

$$r = \frac{[E_0]K_2[S]}{K_m\left(1 + \frac{k_a}{H^+} + \frac{[H^+]}{K_b}\right)}$$

NOTE

If we study the reaction at low pH $\frac{[H^+]}{K_b}$ is very high.

Equation (1) becomes, $r = \frac{k_2[E_0][S]}{K_m\left(\frac{H^+}{K_b}\right)}$ ------(2)

$$r = \frac{k_2 k_b [E_0][S]}{K_m[H^+]} \rightarrow (3)$$

Taking log for equation (3)

log r = constant – log[H^+]

log r = Const + pH   is at low pH .

(ii) At intermediate P^H the k_m value cannot be neglected from equation (1)

$r = \frac{k_2[E_0][S]}{K_m}$ ---- (4) pH has no effect on rate

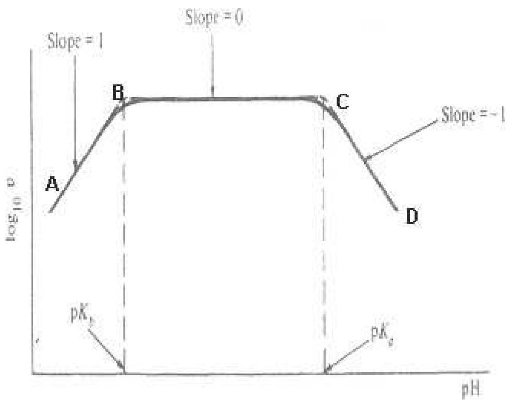
(iii) At high pH value the term k_a/H^+ is large in equation (1)

$$r = \frac{K_2[E_0][S]}{K_m\left(1 + \frac{k_a}{H^+} + \frac{[H^+]}{K_b}\right)}$$

$r = \frac{K_2[E_0][S]}{K_m \frac{k_a}{H^+}}$ ------- (4a)

log r = Constant + logH^+

log r = Constant – pH → (5)



NOTE

In the graph AB has +ve slope satisfy the eqn (3a)

BC is by equation (4)

CD is by equation (5)

At point B the eqn (3a) and (4) are equal

$$\frac{k_2[E_0][S]}{K_m H^+} = \frac{k_2[E_0][S]}{K_m}$$

$$[H^+] = K_b$$

pH = PK_b

At point 'C' the equation (4) and (4a) are equal

$$\frac{k_2[E_0][S]}{K_m} = \frac{k_2[E_0][S][H^+]}{K_m k_a}$$

$$[H^+] = Ka, \quad P^H = pKa$$

14.8 INFLUENCE OF TEMPERATURE

At temperatures of 35°C or higher the enzyme may undergo

Rapid deactivation during the course of a kinetic experiment and then low rate of transformation of a substrate is observed.

Generally the rates of enzyme catalyzed reaction frequently pass through a maximum as the temperature is raised. The temperature at which the rate is maximum often referred to as the maximum temperature (optimum temperature).

At low temperature no appreciable inactivation occurs or by making correction for the inactivation, it is possible to determine the effect of temperature on enzyme catalyzed reaction itself.

$$r = \frac{k_2[E_0][S]}{[s] + K_m}$$

(i) At high concentration of [s]

$$r = k_2 [E_0]$$

$$K_2 = Ae^{-\frac{\varepsilon a}{RT}}, \ln r = \ln k_2 + \ln E_0$$

$$\ln r = \ln AE_0 - \frac{E_a}{RT}$$

High the energy of activation lower the rate

(ii) At low concentration of substrate

$$r = \frac{k_2}{k_m}[E_0][S]$$

$$r = \frac{k_1 k_2}{k_{-1} + k_2}[E_0][S]$$

If $K_{-1} >> K_2$

$$r = \frac{k_1 k_2}{k_{-1}}[E_0][S]$$

The energy of activation is now equal to $E_1 + E_2 - E_{-1}$.

14.9 Check Your Progress

1. What is meant by Acid base catalyst?
2. Explain PH effect.

14.10 Answers To Check Your Progress Questions

1. In acid-base catalysis, the chemical reaction is accelerated by the addition of an acid or a base, and the acid or base itself is not consumed in the reaction. ... Proton donors and acceptors, i.e. acids and base may donate and accept protons in order to stabilize developing charges in the transition state

2. Enzymes are affected by changes in pH. The most favorable pH value - the point where the enzyme is most active - is known as the optimum pH. This is graphically illustrated in Figure 14. Extremely high or low pH values generally result in complete loss of activity for most enzymes

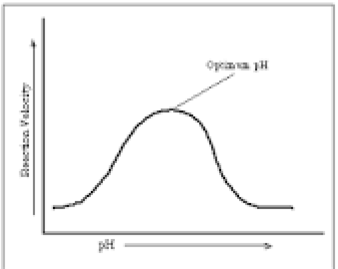


FIGURE 14
Effect of pH on reaction rate

14.11 Summary

- General catalysis is indicated when the rate of the reaction depends upon the concentration of the

NOTE

buffer as well as the pH of the solution, it is most likely to be observed when the pH of the solution is near the pKa of the buffer, and the reaction mechanism involves proton transfer in the rate-determining step.

- The PH effect causes polydentate complexes to be thermodynamically more stable than their monodentate counterpart

14.12 Keywords

Acid base catalysts: In **acid-base catalysis**, the chemical reaction is accelerated by the addition of an **acid** or a **base**, and the **acid** or **base** itself is not consumed in the reaction..... Proton donors and acceptors, i.e. **acids** and **base** may donate and accept protons in order to stabilize developing charges in the transition state

PH pH is a measure of hydrogen ion concentration, a measure of the acidity or alkalinity of a solution. The **pH** scale usually ranges from 0 to 14. Aqueous solutions at 25°C with a **pH** less than 7 are acidic, while those with a **pH** greater than 7 are basic or alkaline PH

14.13 Self-assessment questions and exercises

1. Discuss the influence of pH and temperature on enzyme catalyzed reactions.
2. Discuss the effect of subsistent on reaction rates in terms of Hammett equation and Taft equation
3. Discuss the effect of ionic strength on reaction rates.

14.14 Further readings

1. Shriver and Atkins., Physical Chemistry, 5th ed : W. H. Freeman and Company New York.
2. C.M. Guldberg and P. Waage,"Studies Concerning Affinity" *Forhandlinger i Videnskabs-Selskabet i Christiania* (1864), 35
3. P. Waage, "Experiments for Determining the Affinity Law" ,*Forhandlinger i Videnskabs-Selskabet i Christiania*, (1864) 92.
4. C.M. Guldberg, "Concerning the Laws of Chemical Affinity", *Forhandlinger i Videnskabs-Selskabet i Christiania* (1864) 111

ALAGAPPA UNIVERSITY DISTANCE EDUCATION
M.Sc. Degree Examination
Advanced Physical chemistry (CBCS 2018 – 19 Academic year onwards)
Time: Three hours Maximum: **75 marks**

NOTE

SECTION A Answer All Questions

(10 X2 = 20)

1) What is simple definition of entropy?
2) How is vibrational partition function calculated?
3) What is difference between Fermi Dirac and Bose Eistein statistics?
4) Write the wave equation formula.
5) Explain the paulis exclusion principle.
6) Give the two application of HMO method.
7) Define point group.
8) Define the reducible and irreducible representations.
9) What is difference between primary and secondary salt effect.
10) Mention the acid base catalysis.

SECTION B Answer ALL questions, choosing either (a) or (b)

(5 × 5 = 25)

11. (a)Write the short notes on negative absolute temperature.
(or)
(b) Mention the equilibrium constant from partition function.

12. (a) Define the approximation and variation methods of quantum mechanical treatments.
(or)
(b) How will you find out the Bose Eistein Distribution law?

NOTE

13. (a) Write the short notes on HMO methods.

(or)

(b) What are character table of C2V and C3 V point groups.

14. (a) Write the applications of group theory of electronic spectra.

(or)

(b) What are the factors affected in reaction rate of solutions?

15. (a) Mention the Hammett and Taft equations.

(or)

(b) What is bronsted relation of acid-base catalysis reactions?

SECTION C Answer any THREE questions (3 × 10 = 30)

16) How is Boltzmann distribution calculated?

17) How do solve the one dimensional wave equation?

18) (a) predict the IR and NMR spectra of H_2O and NH_3 molecules.

(b) Define point groups, and mention the classification of point groups.

19) Explain the Bronsted Bjerrum equation.

20) Explain the following

a. Zuker Hammet equation

b. Michaelis Menton Equation

c. Lineweaver-Burke Equation.